ИЗВЕСТИЯ
АКАДЕМИИ НАУК СССР
ОТДЕЛЕНИЕ
ХИМИЧЕСКИХ НАУК

Number 3

March 1958

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

Division of Chemical Science

(IZVESTIIA AKADEMII NAUK SSSR)

(Otdelenie Khimicheskikh Nauk)

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU, INC.

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

(Division of Chemical Science)

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A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:
no. 1 *Jan.-Feb. 1952*

	U. S. and Canada	*Foreign*
Annual subscription	*$45.00*	*$50.00*
Annual subscription for libraries of non-profit academic institutions	*15.00*	*20.00*
Single issue	*5.00*	*5.00*

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1958, No. 3 March

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STUDY OF THE PROPERTIES OF INDIUM HYDROXIDE, AND THE SEPARATION OF INDIUM FROM ZINC

E. N. Deichman

In our previous paper on the formation of indium hydroxide [1] we gave results on the physicochemical analysis of the systems $InCl_3 - NaOH - H_2O$ and $In_2(SO_4)_3 - NaOH - H_2O$, and established the formation of two basic salts $In(OH)_{2.8}Cl_{0.2}$ and $In(OH)_{2.5}(SO_4)_{0.25}$ and of indium hydroxide $In(OH)_3$. We considered it to be of interest to determine the behavior of indium hydroxide in solutions of alkali at various concentrations in order to explore the possibility of, and to establish the most effective conditions for, the separation of indium from various other elements, e.g., beryllium, zinc, aluminum, gallium, germanium, tin, lead, chromium, and molybdenum, which form soluble compounds with excess of alkali.

It is known from the literature that the dissolution of the hydroxides of most of the elements enumerated above requires a considerable excess of alkali above the stoichiometric amount. References to the ability of indium hydroxide to dissolve in solutions of alkali-metal hydroxides are first met in the papers of Winkler [2]. Later, Renz [3] noted the formation of salts of indic acid, which he named indates and represented by the formula $InO-OH$. Lacroix [4] also states that indates are formed in a strongly alkaline medium, and he represents them by the formula $NaInO_2$. Ivanov-Emin and Ostroumov [5] obtained hydroxoindates from a boiling 60% solution of sodium hydroxide. The composition of the compound isolated corresponded to the formula $Na_3[In(OH)_6] \cdot 2H_2O$. The authors state that under the action of traces of water this compound decomposes very rapidly with formation of sodium and indium hydroxides.

As will be seen from this review of the literature, the behavior of indium hydroxide in alkali-metal hydroxide solutions has received inadequate study. The object of the present work was to establish the character of the chemical interaction between indium hydroxide and sodium hydroxide solutions of various concentrations.

EXPERIMENTAL

The preparation of the original solutions of indium chloride and sulfate and of sodium hydroxide were described in our previous paper [1]. It must be pointed out that the determination of indium by precipitation with ammonia in presence of large amounts of salts, in this case NaCl, formed in the neutralization is made considerably more difficult owing to the enhanced solubility of $In(OH)_3$ under these conditions, as a result of which low yields are obtained. Satisfactory results are obtained when the following procedure is used. Hydrochloric acid was added to the centrifugate (50 ml) until it was neutral to methyl orange, and this was followed by excess (10 drops) of 25% ammonia. The solution was then heated for two hours in a water bath; the precipitate of indium hydroxide was filtered off, washed, and calcined to In_2O_3. When the content of indium was low, it was determined colorimetrically [6] from the color formed with diphenylamine in presence of potassium ferrocyanide. The results are given in Tables 1 and 2.

It is easily seen from the results that the solubility of indium in NaOH solutions is very slight. Even in very concentrated NaOH solutions (8 M), the indium content is $1 \cdot 10^{-3}$ mole/liter. In the concentration range 4-8 M NaOH the solubility of indium remains almost constant. Experiments on the determination of indium in 8 M alkali after various periods of time gave the following results (Table 1). The indium contents after three and six days were $2.7 \cdot 10^{-3}$ and $1.6 \cdot 10^{-3}$ mole/liter, respectively. After nine days the indium contents of 8 M and 4 M solutions were almost identical and equal to $2.3 \cdot 10^{-3}$ mole/liter. Hence, in considering the solubility of indium hydroxide in alkali solutions, we must take account of the time for which the solution has stood.

The presence of sulfate ions in the solution has a small effect on the solubility of indium hydroxide. As in the previous system, the solubility of indium hydroxide varies little with increase in alkali concentration. It is almost the same in 4 M and 8 M solutions and is about $1 \cdot 10^{-3}$ mole of indium per liter (Table 1). The peptization of the precipitate of indium hydroxide under the action of NaOH solutions is much less notable in the $In_2(SO_4)_3$ system. In the second case the solutions obtained after saturation were generally more turbid, took longer to settle, and required more prolonged centrifugation than solutions obtained by treating indium sulfate with alkali. The results that we have reported indicate that in treatments with concentrated solutions of alkali under our conditions no appreciable formation of indates occures in the solid phase. The extremely low solubility of indium hydroxide, about $1 \cdot 10^{-3}$ mole/liter, raises doubt about the existence of stable $In(OH)_6^{3+}$ ions, the formation of which should be accompanied by appreciable increase in the solubility of indium.

TABLE 1

Solubility of Indium Hydroxide in NaOH Solutions of Various Concentrations (Original Indium Salt Solution 0.01 mole/liter)

In original mixture NaOH/ / $InCl_3$	Amount of In^{3+} found in sat. sol. above precipitate (g-ion/liter)	In original mixture 2NaOH/ / $In_2(SO_4)_3$	Amount of In^{3+} found in sat. sol. above precipitate (g-ion/liter)
10	—	10	—
20	—	20	—
50	0,00005	50	0,000015
100	0,0001	100	0,00026
200	0,0002	200	0,00014
400	0,0020	300	0,00025
600	0,0020	400	0,0012
800	0,0027	600	0,0010
800	0,0018	800	0,0016
800	0,0018		

TABLE 2

Solubility in the System $ZnSO_4(ZnCl_2)-NaOH-H_2O$ at 25°
(Original $ZnSO_4$ and $ZnCl_2$ solutions 0.01 mole/liter)

In original mixture NaOH/ / $ZnSO_4$	Amount of Zn^{2+} found in saturated solution above precipitate (g-ion/liter)	In original mixture NaOH/ / $ZnCl_2$	Amount of Zn^{2+} found in sat. sol. above precipitate (g-ion/liter)
0,6	0,0053	0,25	0,0087
0,8	0,0036	0,50	.0,0073
1,1	0,002	0,75	0,0066
1,4	0,0001	1,0	0,0054
1,7	Absent	1,5	0,0022
1,9	»	1,7	0,0008
2,0	»	1,8	0,0006
4,0	»	1,9	Absent
5,0	»	2,0	»
6,0	$1,0 \cdot 10^{-5}$	4,0	»
10,0	0,002	5,0	»
20,0	0,008		
23,0	0,009		
25,0	0,0094		
30,0	A little crystalline precipitate forms after 58 hours		
50,0	Absent		

Experiments were carried out also on the effect of the order of mixing solutions of the solubility of $In(OH)_3$ in alkaline solutions. When an indium salt was added to NaOH solutions, these remained clear for five minutes, then became turbid and yielded a precipitate. When the solutions of indium salts were added rapidly to the alkali, the solutions remained clear for a much longer time (20-30 minutes), after which a precipitate formed. After the system had been stirred in a thermostat, the indium content of the saturated solution became identical with the values found previously (about $1 \cdot 10^{-3}$ mole/liter). This indicates that the indates formed are extremely unstable and decompose rapidly with formation of indium hydroxide. As regards insoluble indates, their preparation in a crystalline form is possible only in those special conditions under which they were isolated by Ivanov-Emin and Ostroumov [5].

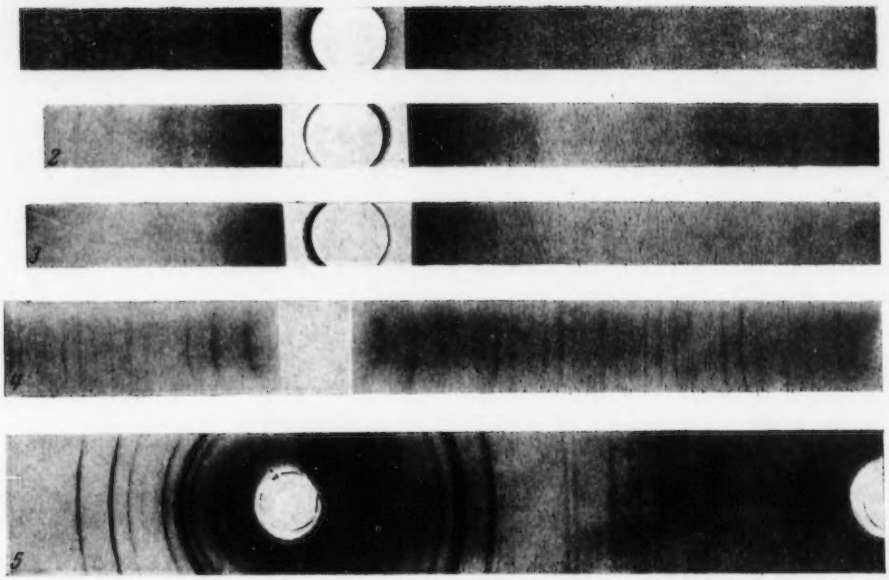

Fig.1. x-Ray diagram of $In_2(SO_4)_3$. Fig. 2. x-Ray diagram of $In(OH)_{2.8}Cl_{0.2}$.
Fig. 3. x-Ray diagram of $In(OH)_{2.5}(SO_4)_{0.2}$. Fig. 4. x-Ray diagram of $In(OH)_3$.
Fig. 5. x-Ray diagram of In_2O_3.

The crystal optics of the solid phases isolated from NaOH solutions of various concentrations were investigated by Buravaia, and the results are presented in Table 3*. The results indicate that the solid phases isolated in presence of a stoichiometric amount of NaOH and from concentrated NaOH solutions are identical, which confirms previous conclusions concerning the nonformation of insoluble indates. x-Ray diffraction photographs taken by Kuznetsov [7] show that for:

$InCl_3$: no x-ray diagram could be obtained, the substances being very hydroscopic and deliquescent in the air.

$In_2(SO_4)_3$: sharp x-ray diagram with characteristic lines (Fig. 1).

$In(OH)_{2.8}Cl_{0.2}$: characteristic and typical x-ray diagram with weak and diffuse lines (Fig. 2).

$In(OH)_{2.5}(SO_4)_{0.25}$: an x-ray diagram similar to that for $In(OH)_3$ isolated in the same system (Fig. 3).

$In(OH)_3$: when this is isolated from equimolecular solutions in the chloride system the x-ray diagram has characteristic, but weak and diffuse lines (Fig. 4).

$In(OH)_3$: when this is isolated from 4 N NaOH (Fig. 5), the x-ray diagram is similar to that given in Fig. 4, but the lines are sharp; the structure is cubic.

$In(OH)_3$: when this is isolated from 6 N NaOH the x-ray diagram is similar to that given in Fig. 4.

These results confirm the conclusion to which we arrived above, namely that the indium hydroxide solid phases isolated at equivalent proportions and in presence of a large excess of concentrated NaOH solution are identical. Our results on the x-ray analysis of indium hydroxide are in accord with data in the literature.

In order to study the thermal decomposition of the basic salts that we had synthesized and of indium hydroxide, we determined heating curves with the aid of a Kurnakov pyrometer, using the method of differential recording. Fig. 6 shows that thermogram of $In(OH)_3$ isolated from mixtures containing equivalent amounts of $InCl_3$ and NaOH.

*The tables are given exactly as in the original; it will be noted that Table 3 is not concerned with crystal optics, neither is Table 1 concerned with the variation of solubility with time as indicated in the text. – Publisher.

As will be seen from the thermogram, the first endothermic effect is due to partial dehydration. When heated to 135°, indium hydroxide loses 5.27% in weight, which corresponds to the loss of one molecule of water. The second endothermic effect corresponds to the loss of the remaining water and the formation of indium oxide. When a sample is heated from 135° to 270° there is a loss in weight of 10.87%, which corrresponds to a loss of two molecules of water. The small exothermic effect at 340° evidently corresponds to recrystallization of the phase on passage from the amorphous modification to the crystalline one. A sharp x-ray photograph was obtained from indium oxide, which has a cubic structure. Heating above 340° gave no thermal effects and did not result in loss of weight.

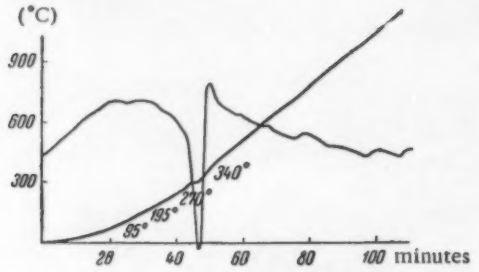

Fig. 6. Thermogram of $In(OH)_3$

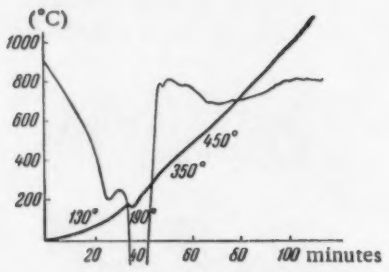

Fig. 7. Thermogram of $In(OH)_{2.8}Cl_{0.2}$

Hence, the reactions occurring in the thermal decomposition of indium hydroxide can be represented as follows:

1. $In_2O_3 \cdot 3H_2O - H_2O \rightarrow In_2O_3 \cdot 2H_2O$.
2. $In_2O_3 \cdot 2H_2O - 2H_2O \rightarrow In_2O_3$.

On the thermogram of $In(OH)_{2.8}Cl_{0.2}$ (otherwise $5In_2O_3 \cdot 13H_2O \cdot 2HCl$) (Fig. 7), there are three endothermic effects. The first effect, a minimum on the differential record, is at 130° and corresponds to the loss of six molecules of water (loss in weight of 6.56%). The second effect (190°) corresponds to the loss of the remaining water. The dehydration results in the formation of indium oxychloride, which decomposes at a higher temperature (350--450°). It was established that chlorine is present in a sample heated to 300°. When it was heated to 450°, all the chlorine was quantitatively removed.

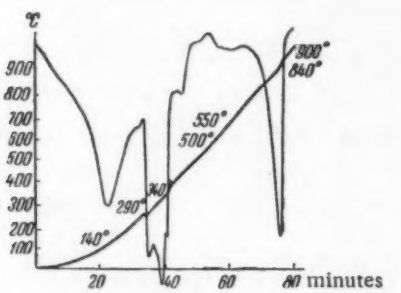

Fig. 8. Thermogram of $In(OH)_{2.5}(SO_4)_{0.25}$

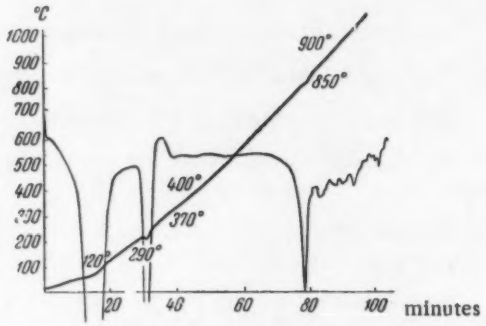

Fig. 9. Thermogram of $In(OH)_3$

Fig. 8 gives the thermogram of $In(OH)_{2.5}(SO_4)_{0.25}$ or $2In_2O_3 \cdot 5H_2O \cdot SO_3$. The three sharp exothermic effects correspond, respectively, to the loss of three molecules of water at 140°, the loss of two molecules of water at 290-340°, and the formation of indium oxide at 840°, which is in accord with the results of analysis. As in the previous case, dehydration was accompanied by change in the structure of the substance and an exothermic effect.

The thermal decomposition of indium hydroxide isolated from 6 N indium sulfate by means of NaOH solution is represented in Fig. 9. The same three endothermic effects can be seen on the thermogram: the loss of one molecule of water at 120°, the loss of two molecules of water at 290°, and the fusion of Na_2SO_4 at 900°. The presence of Na_2SO_4 is to be explained by its adsorption by the indium hydroxide precipitate, which was not washed, but merely

pressed off from the mother liquor. Fig. 10 gives the thermogram of the same sample after three washes with water. In this case the effect due to the fusion of Na_2SO_4 is insignificant. On this thermogram the exothermic effect due to change in crystal structure is very notable.

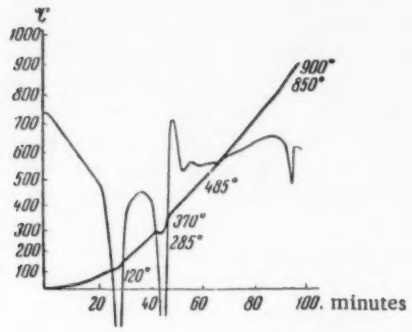

Fig. 10. Thermogram of $In(OH)_3$

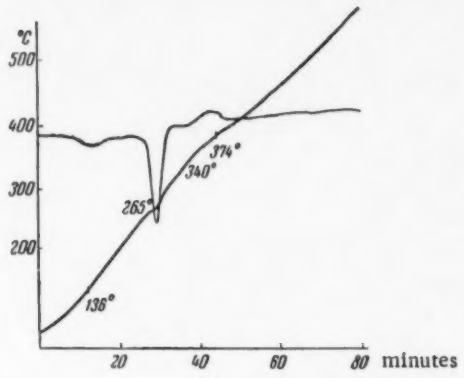

Fig. 11. Thermogram of $In(OH)_3$

For comparison purposes, in Fig. 11 we give the thermogram of indium hydroxide precipitated with ammonia from indium chloride and carefully washed with water. Apart from two endothermic and one exothermic effect, no thermal effects were to be observed. As will be seen from the results, the loss of water by all these compounds occurs in the temperature range 120-350°. In comparing the temperature of total decomposition of $In(OH)_3$, $In(OH)_{2.8}Cl_{0.2}$ and $In(OH)_{2.5}(SO_4)_{0.25}$, we may note the following sequence for the removal of water: $In(OH)_3$ decomposes at 340° with formation of In_2O_3; $In(OH)_{2.8}Cl_{0.2}$ decomposes at the higher temperature 450°, and $In(OH)_{2.5}(SO_4)_{0.25}$ naturally decomposes at a still higher temperature (about 550°).

DISCUSSION OF RESULTS

A comparison of the results obtained in the study of solubility in the ternary systems $InCl_3-NaOH-H_2O$ and $In_2(SO_4)_3-NaOH-H_2O$ enables us to establish that in both systems indium hydroxide has a very low solubility in concentrated solutions of caustic alkali. The solubility of $In(OH)_3$ in sodium hydroxide solutions (from 4 M to 8 M). is almost constant. Our experimental results indicate that no stable soluble or insoluble indates are formed in these systems even in concentrated NaOH solutions. In this respect indium hydroxide differs substantially from both aluminum and gallium hydroxides.

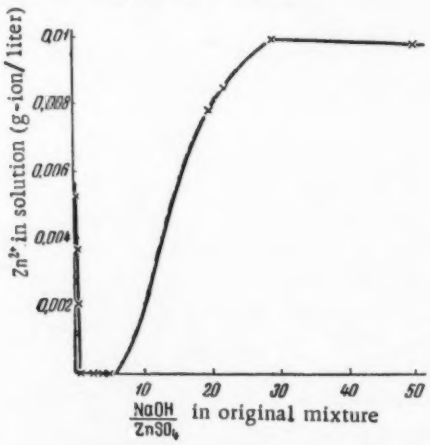

Fig. 12. Solubility in the system $ZnSO_4-NaOH-H_2O$

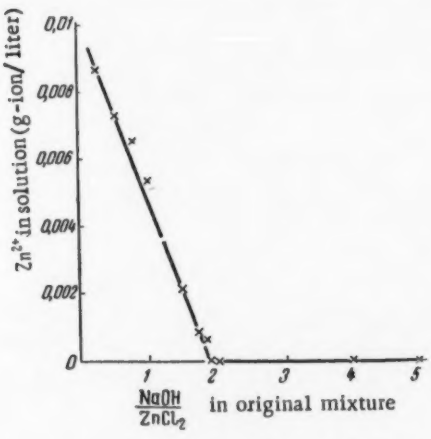

Fig. 13. Solubility in the system $ZnCl_2-NaOH-H_2O$

By crystal optics and x-ray analysis we have established the individuality of basic indium salts and the identity

of the indium hydroxide precipitates isolated from equimolecular and 6 M solutions of sodium hydroxide, which again points to the nonformation of insoluble indates in the system. The results indicate the immutability of indium hydroxide in concentrated solutions of caustic alkali, and this makes it possible to separate indium from various elements which form soluble compounds in alkaline solutions.

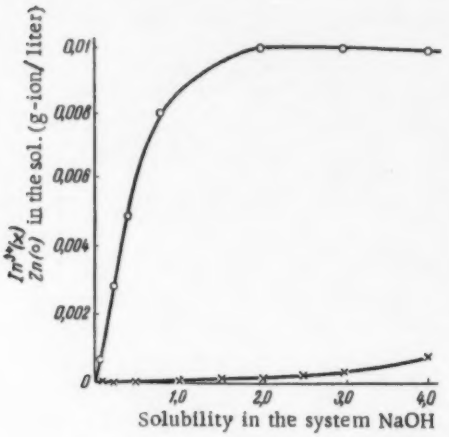

Fig. 14. Solubility in the system $In_2(SO_4)_3-ZnSO_4-NaOH-H_2O$.

Below we describe the results of the separation of indium and zinc by a method based on this principle. We first carried out experiments on solubility in the systems $ZnSO_4-NaOH-H_2O$ and $ZnCl_2-NaOH-H_2O$. The procedure was the same as that used in the study of similar indium systems [1]. From the data given in Table 2 and Figures 12 and 13 it will be seen that zinc is completely precipitated from 0.01 M $ZnSO_4$ in the form of the basic salt. Further addition of NaOH until the ratio of NaOH : $ZnSO_4$ = 2.0 results in the formation of zinc hydroxide. The $Zn(OH)_2$ begins to dissolve when six equivalents of alkali have been added. Addition of 30 equivalents of NaOH results in complete dissolution of $Zn(OH)_2$, but after 48 hours a coarsely crystalline precipitate forms, and only after the addition of 50 equivalents of NaOH do the solutions remain clear for a long time without the separation of a precipitate of zinc hydroxide even after one month's standing.

Solubility in the system $ZnSO_4-NaOH-H_2O$ was studied by Tananaev and Mzareulishvili [8]. Our results are similar to theirs. These authors found that in the addition of NaOH to 0.025 M $ZnSO_4$ the zinc passes completely into solution at a ratio of NaOH : $ZnSO_4$ = 10. Some discrepancies with respect to our results are possibly to be explained by the fact that these authors used different original concentrations of zinc sulfate. The precipitation of hydroxide from zinc chloride solution differs considerably from the case of sulfate. The nature of the anion of the salt is of considerable significance in the formation of the basic salt. Complete precipitation of zinc from solution occurs when 1.9 equivalents of alkali have been added. The addition of two equivalents of NaOH is accompanied by the formation of $Zn(OH)_2$. At a ratio OH^- : Zn^{2+} = 20 the appearance of the precipitate changes sharply and, as in the previous system, it forms glistening transparent crystals, firmly attached to the walls of the vessel. The precipitate evidently corresponds to the formation of a new much more soluble modification of $Zn(OH)_2$, because the formation of a crystalline zincate in 0.2 M NaOH is not very likely. As can be seen from our results, the formation of zincate in both systems occurs when the alkali is present in large excess. In order to establish the

TABLE 3

Solubility in the System $In_2(SO_4)_3 - ZnSO_4 - NaOH - H_2O$ at 25° (original $In_2(SO_4)_3$ solution 0.01 mole/liter)

Amount of orig. mixture taken (mole/liter)		Amount found in saturated solution (g-ion/liter)		Amount of orig. mixture taken (mole/liter)		Amount found in saturated solution (g-ion/liter)	
NaOH	$ZnSO_4$	In^{3+}	Zn^{2+}	NaOH	$ZnSO_4$	In^{3+}	Zn^{2+}
0,02	0,01	0,0021	0,0096	1,00	0,01	$5\cdot10^{-5}$	0,0081
0,04	0,01	Absent	0,0036	1,50	0,01	$7\cdot10^{-5}$	0,0084
				2,00	0,01	$8\cdot10^{-5}$	0,0090
0,05	0,01		Absent	2,50	0,01	$1,2\cdot10^{-4}$	0,0097
				3,00	0,01	$2\cdot10^{-4}$	0,0100
0,06	0,01	»	»	4,00	0,01	$1\cdot10^{-3}$	0,0100
0,10	0,01	»	»	3,19	0,08	$1,9\cdot10^{-4}$	0,0800
0,15	0,01	»	0,0008	2,50	0,09	$1,5\cdot10^{-4}$	0,0893
0,25	0,01	»	0,0029	3,21	0,09	$1,9\cdot10^{-4}$	0,0898
0,50	0,01	»	0,0050				

optimum conditions for the separation of indium from zinc, a study was made of solubility at 25° in the systems:

$In_2(SO_4)_3 - ZnSO_4 - NaOH - H_2O$ and $InCl_3 - ZnCl_2 - NaOH - H_2O$

The following method was used: solutions of indium and zinc salts and of sodium hydroxide (all of known titer) were introduced into hermetically closed 100-ml vessels, and water was added in such amount that the original mixtures contained 0.01 mole/liter of indium salt, 0.01 mole/liter of zinc salt, and various amounts of NaOH ranging from 0.02 M to 4.00 M. The mixtures were agitated in a thermostat (25 ± 0.1°) for six hours and were then allowed to settle.

The zinc, indium, and sodium hydroxide contents of the saturated solution were determined. Indium was determined in presence of zinc with the aid of pyridine [9], and very small amounts were determined polarographically [10]. The results are given in Table 3 and 4 and in Figs. 14. and 15. The results show that in the indium sulfate system at low concentrations (0.02 M) of sodium hydroxide, indium is precipitated almost completely in the form of the basic salt and zinc remains in solution. In 0.04 M NaOH indium is precipitated quantitatively as hydroxide and zinc is partially precipitated as basic salt.

In 0.05 M NaOH indium and zinc are precipitated as hydroxides. Further increase in NaOH concentration results in dissolution of zinc hydroxide. The results indicate that the presence of the indium salt in the solution considerably reduces the tendency for zinc hydroxide to dissolve in alkali. In the ternary system $Zn(OH)_2$ begins to dissolve in 0.06 M NaOH, but in presence of indium salt the start of zincate formation corresponds to 0.15 M NaOH and the quantitative dissolution of zinc hydroxide starts only at 3.00 M NaOH, which is ten times the amount of NaOH necessary for the dissolution of $Zn(OH)_2$ in absence of indium. In presence of concentrated solutions of NaOH (1.0 M and higher concentrations) partial dissolution of indium hydroxide occurs. In 3.00 M NaOH it dissolves to the extent of $2 \cdot 10^{-4}$ mole/liter.

TABLE 4

Solubility in the System $InCl_3 - ZnCl_2 - NaOH - H_2O$ at 25°. (original $InCl_3$ solution 0.01 mole/liter).

Amount taken in orig. mix. (mole/liter)		Amount found in saturated solution (g-ion/liter)		Amount taken in orig. mix. (mole/liter)		Amount found in saturated solution (g-ion/liter)	
NaOH	$ZnCl_2$	In^{3+}	Zn^{2+}	NaOH	$ZnCl_2$	In^{3+}	Zn^{2+}
0,03	0,01	Colloidal solution		1,20	0,01	$8 \cdot 10^{-5}$	0,0077
0,04	0,01	0,0001	0,0045	2,00	0,01	$9 \cdot 10^{-5}$	0,0082
0,046	0,01	Absent	Absent	2,50	0,01	$1 \cdot 10^{-4}$	0,0096
				3,00	0,01	$4 \cdot 10^{-4}$	0,0099
0,05	0,01	»	»	1,50	0,05	$5 \cdot 10^{-5}$	0,0450
0,06	0,01	»	»	2,00	0,05	$8 \cdot 10^{-5}$	0,0482
0,08	0,01	»	»	2,55	0,05	$1,2 \cdot 10^{-4}$	0,0498
0,10	0,01	»	»	3,05	0,05	$4,0 \cdot 10^{-4}$	0,0502
0,20	0,01	»	»	1,00	0,1	Absent	0,0260
0,40	0,01	»	0,006	1,50	0,1		0,0960
0,50	0,01	»	0,007				
0,60	0,01	»	0,008	2,0	0,1	$2 \cdot 10^{-4}$	0,0970
1,00	0,01		0,0072	3,20	0,1	$6 \cdot 10^{-4}$	0,1008

Experiments with a mixture of 0.09 mole/liter of zinc salt and 0.01 mole/liter of indium salt also showed the necessity for the presence of free alkali in the solution at a concentration of 3.00 M for quantitative separation of the elements. Quite analogous results were obtained in the study of solubility in the system $InCl_3 - ZnCl_2 - NaOH - H_2O$. Low NaOH concentrations result in quantitative precipitation of indium and partial precipitation of zinc in the form of the basic salt. In 0.046 M NaOH indium and zinc are precipitated quantitatively. For the

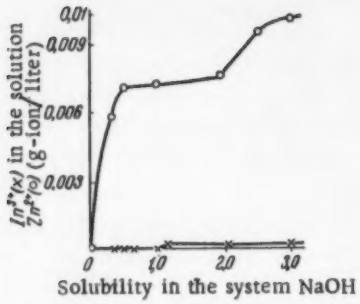

Fig. 15. Solubility in the system $InCl_3 - ZnCl_2 - NaOH - H_2O$.

start of dissolution of zinc hydroxide with formation of zincate a much greater excess of alkali is required than in the previous system; it begins in 0.4 M NaOH. The quantitative formation of zincate in presence of indium chloride at 0.01, 0.05, and 0.10 M again requires an excess of NaOH on 3.00 moles/liter. Further increase in alkali concentration results in considerable increase in the solubility of indium hydroxide for the same content of zinc in the solution. A very marked effect on the solubility of zinc hydroxide is exerted by the presence of carbon dioxide, which reduces it to such an extent that the zinc hydroxide is not completely dissolved even in 5.0 M NaOH, some of it (about 10%) remaining in the precipitate with the indium hydroxide.

SUMMARY

1. A study was made of the solubility of indium hydroxide in sodium hydroxide solutions of various concentrations (0.1-8.0 M).

2. It was found that the solubility of indium hydroxide in concentrated NaOH solutions does not exceed $2 \cdot 10^{-3}$ mole/liter.

3. It was shown that in the systems studied, $InCl_3-NaOH-H_2O$ and $In_2(SO_4)_3-NaOH-H_2O$, no stable soluble or insoluble indates are formed.

4. Analysis by crystal optics and x-ray diffraction confirmed the individuality of the basic indium salt and the identity of the various indium hydroxide precipitates, irrespective of the concentration of alkali in the system.

5. The basic salts and indium hydroxide were submitted to thermographic analysis.

6. A study was made of solubility in the systems $ZnSO_4-NaOH-H_2O$; $ZnCl_2-NaOH-H_2O$; $In_2(SO_4)_3 - -ZnSO_4-NaOH-H_2O$; $InCl_3-ZnCl_2-NaOH-H_2O$. The optimum conditions for the separation of indium and zinc in the form of hydroxides were established.

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Received February 3, 1957

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RELATION BETWEEN THE CATALYTIC ACTIVITY OF BINARY COMPOUNDS OF GROUP II METALS WITH NONMETALS AND THE POSITIONS OF THE ELEMENTS IN MENDELEEV'S PERIODIC SYSTEM

COMMUNICATION 3. CATALYTIC DECOMPOSITION OF ISOPROPYL ALCOHOL OVER SULFIDES OF GROUP II METALS

O. V. Krylov and E. A. Fokina

The number of systematic kinetic investigations that have been devoted to the catalytic properties of sulfides is relatively small, particularly when compared with the number of investigations of this type devoted to oxides and metals. In particular, there have been only a few investigations on the catalytic activity of sulfides of Group II metals. Most of these have been carried out with zinc sulfide, which has been studied as a catalyst for the dehydrogenation of ethylbenzene and of ethanol [1, 2], for the decomposition of methanol [3, 4], for the decomposition of hydrogen peroxide [5], and for other reactions.

The present work forms part of a systematic investigation of the catalytic properties of binary compounds of Group II metlas with nonmetals of Group VI [6, 7]. Apart from sulfides of Group II metals (Zn, Cd, Hg), we studied a few samples of sulfides of metals of other groups (Pb, Bi). Detailed results of an investigation on the stability of the sulfides that we have studied, in which radiosulfur S^{35} was used, are reported in one of our previous papers [8].

EXPERIMENTAL

The sulfides studied were as follows:: Zinc sulfide, ZnS, chemically pure grade and a product obtained by precipitation from $ZnSO_4$ solution with freshly prepared ammonium sulfide; Cadmium sulfide, CdS, chemically pure grade and a product obtained by precipitation from $CdSO_4$ solution with freshly prepared ammonium sulfide; Mercuric sulfide, HgS, commercially obtained red and black forms and a product obtained by precipitation from $Hg(CH_3COO)_2$ solution with H_2S; Lead sulfide, PbS, obtained by precipitation from $Pb(CH_3COO)_2$ solution with H_2S; Bismuth sulfide, Bi_2S_3, obtained by precipitation from $Bi(NO_3)_3$ solution with H_2S. We prepared also samples of ZnS, CdS, and PbS labeled with radiosulfur S^{35} and of ZnS and CdS with additions of the corresponding sulfates $ZnSO_4$ and $CdSO_4$ labeled with radiosulfur S^{35}. For the method of preparing the labeled sulfides see our previous paper [8].

For these sulfides, as in the case of the oxides, we studied the dehydrogenation and dehydration of isopropyl alcohol. Our procedure in the catalytic investigations has been described previously [6, 7]. The acid-base properties of the catalysts were measured by the method that we have developed [9].

Table 1 gives the results of the experiments on the catalytic decomposition of isopropyl alcohol in a flow system at atmospheric pressure in the order in which they were carried out. The values given correspond to the stationary state, which was usually established in the course of 0.5-2 hours.

The activation energy for dehydration was not calculated, for, as Table 1 shows, in most cases the propene content of the outgoing gases was very low and the accuracy of the calculation would be low. The activation energy for dehydrogenation was calculated from graphs showing the temperature-dependence of the logarithm of the rate of gas liberation (Fig. 1). As pointed out in a previous paper [7], calculations of this kind can be used

TABLE 1

Decomposition of Isopropyl Alcohol over Sulfides and Certain Other Catalysts

Catalyst	Specific surface (sq.m/g)	Temperature (°C)	Average rate of gas liberation (ml per min per ml of alcohol)	Propene content of gas	Activation energy for dehydrogenation E (cal/mole)
ZnS, chemically pure	4,0	312	162	2,0	
		328	227	4,4	
		352	327	4,5	
		228	8,7	0	18 000
		254	27	0,4	
		282	56	1,2	
		312	151	1,2	
ZnS, chemically pure (another sample)		252	67	1,5	
		282	130	1,0	
		310	202	1,5	
		326	231	0,3	15 500
		310	194	1,5	
		228	23	1,5	
		306	210	2,1	
After passage of air		306	123	6,6	
		306	133	6,6	
After passage of H_2S		302	46	5,5	
		302	106	4,5	
		308	122	4,0	
ZnS obtained by reaction of $ZnSO_4 + (NH_4)_2S$	145	208	11,6	0,5	
		236	47	1,8	
		260	107	4,0	
		280	222	4,5	17 000
		308	262	7,8	
		254	105	3,6	
CdS, chemically pure		206	34	1,7	
		228	54	1,3	
		252	92	1,2	
		278	143	1,5	11 000
		306	240	3,4	
		288	155	1,1	
		232	62	1,0	
After passage of air		228	28	—	
ZnS obtained by reaction of $ZnSO_4 + (NH_4)_2S$		274	297	24,4	
		248	181	18,9	
		226	45	12,4	20 500
		202	13,1	7,1	
ZnS labeled with S^{35}	108	242	102	10,2	
		266	184	10,4	15 500
		306	277	10,3	
		242	88	9,5	
CdS labeled with S^{35}	47	190	2,6	2,1	
		228	15	2,1	17 000
		246	98	4,1	
		282	168	5,0	
HgS, chemically pure	<3	294	1,5	0	
		368	6,3	0	
ZnS + 2% ZnSOR labeled with S^{35}	101	248	69	38,6	
		270	163	40,4	17 000
		294	211	38,0	
ZnS + 2% $ZnSO_4$ labeled with S^{35}		252	40	11,0	
(another sample)		272	133	13,2	
		310	266	16,0	16 000
		338	354	20,6	

TABLE 1 (Continued)

Catalyst	Specific surface (sq. m/g)	Temperature (°C)	Average rate of gas liberation (ml per min per ml of alcohol)	Propene content of gas	Activation energy for dehydrogenation E (cal/mole)
HgS precipitated from $Hg(CH_3COO)_2$		362	1,2	0	
		392	5,0	3,3	
CdS + 2% $CdSO_4$ labeled with S^{35}	84	234	28	1,1	
		255	111	7,9	17 000
		288	186	13,0	
		310	293	15,5	
PbS labeled with S^{35}		252	4,0	0	
		280	11,0	8,7	
		302	48	32	20 000
		326	76	40,4	
		354	181	42,6	
After passage of air		354	162	41,2	
		332	64		
		330	47		
$PbSO_4$ labeled with S^{35}		298	8,8	8,7	
		332	50	18,8	
		350	70	22,2	27 000
PbO		382	137	27,6	
		244	20	4,6	
		280	61	3,2	19 000
		304	126	2,8	

when the reaction kinetics are approximately of first order. We must point out, however, that in some cases rise in temperature was accompanied by some poisoning of the surface of the sulfides, which in the case of PbS was considerable. Thus, in the experiment with ZnS (see first experiment in Table 1), after the catalyst had worked at high temperatures (3-4 hours at each temperature) and had returned to the initial temperature, its activity had fallen by 7%. The catalytic acitivity of cadmium sulfide was more stable. The changes in the activity of the catalyst during reaction and the departures from first-order kinetics could, as calculation showed, lead to errors in the determination of E of 3-4 kcal/mole, the resulting values generally being too low.

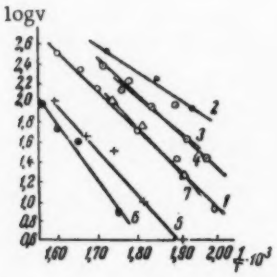

Fig. 1. Relation of the logarithm of the rate of gas liberation to the reciprocal of the temperature for various catalysts: 1) ZnS; 2) CdS; 3) ZnS ppt. from $ZnSO_4$; 4) CdS ppt. from $CdSO_4$; 5) PbS; 6) $PbSO_4$; 7) PbO.

Over most of the sulfide catalysts dehydrogenation of alcohol predominated under the conditions studied. Only in the case of one sample of ZnS obtained by reaction of $ZnSO_4$ with $(NH_4)_2S$ did the propene content of the reaction products attain 24.4% at 274°. A high propene content was observed also over PbS, but at high temperatures (326°). With rise in temperature there was a tendency for the propene content of the gas to increase in the case of several preparations. The activation energies for dehydrogenation over samples of a given catalyst obtained by different methods generally varied considerably (in the range 15,500-20,500 cal/mole in the case of ZnS and 11,000-17,000 cal/mole in the case of CdS), but the main differences in catalytic activity were associated with the values of the specific surface and the pre-exponential term in the Arrhenius equation. Samples of ZnS (chemically pure and prepared by precipitation with ammonium sulfide) showed a 35-fold variation in specific surface, but the activity per square meter of surface showed only a four- to five-fold variation.

Passage of air through the catalysts at high temperature resulted in a sharp fall in catalytic activity and increase in the content of unsaturated hydrocarbons in the gas. Addition of sulfate also resulted in a considerable increase in the extent of dehydration, and at the same time the activity of the catalyst fell somewhat. The activity of pure lead sulfate was less than that of lead sulfide, both for dehydrogenation and for dehydration. Passage of hydrogen sulfide through the catalysts resulted in severe poisoning, but treatment of the catalysts with fresh isopropyl alcohol rapidly reestablished the original activity.

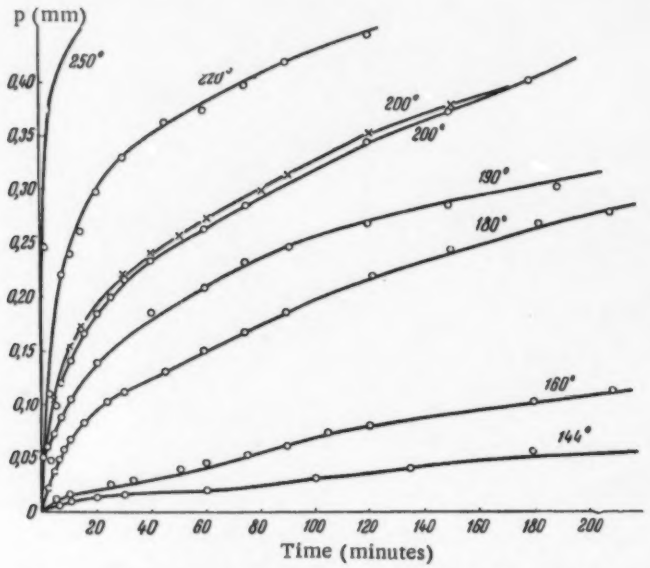

Fig. 2. Kinetic curves for the decomposition of isopropyl alcohol in a surface layer on zinc oxide, the reaction products being frozen out with solid CO_2.

Lead oxide had somewhat higher activity and dehydrogenating power than lead sulfide. Bithmuth sulfide Bi_2S_3, like bismuth oxide Bi_2O_3, though it had high activity at low temperatures and decomposed the alcohol very rapidly at 200°, was poisoned irreversibly and very rapidly as a result of reduction of the surface.

TABLE 2

Composition of the Products of the Decomposition of Isopropyl Alcohol over ZnO

Temp. (°C)	Pressure of reaction product after freezing-out (mm)		Composition of products on assumption of two parallel reactions		Calculated sum of concentrations $2[H_2] + 2[C_3H_6]$	Pressure of products without freezing-out
	with liquid N_2	with solid CO_2	Concn. of H_2 = concn. of C_3H_6O	Concn. of C_3H_6 = concn. of H_2O		
144	0.015	0.064	0.016	0.032	0.096	0.120
160	0.025	0.107	0.025	0.057	0.164	0.177
180	0.062	0.223	0.062	0.099	0.322	0.330
200	0.117	0.326	0.117	0.109	0.452	0.442
220	0.202	0.429	0.202	0.127	0.658	0.648

The kinetics of the decomposition of isopropyl alcohol in the adsorption layer were studied over zinc oxide and zinc sulfide. Fig. 2 gives curves for the rise in pressure in a definite volume, into which the products of the decomposition of the alcohol over ZnO were pumped, water being frozen out with solid CO_2 (−78°). If the view

that the decomposition of isopropyl alcohol proceeds in two directions is correct, then, after freezing-out with liquid N_2 (−195°), only hydrogen should remain in the gas phase. The results of analysis of the reaction products by the freezing-out method are given in Table 2.

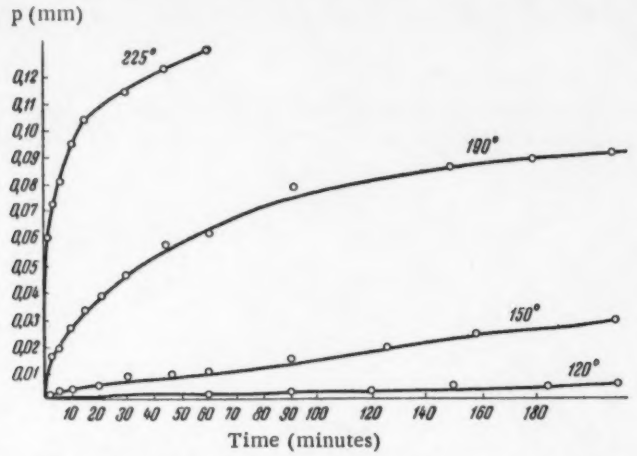

Fig. 3. Kinetic curves for the dehydrogenation of isopropyl alcohol in a surface layer on zinc oxide

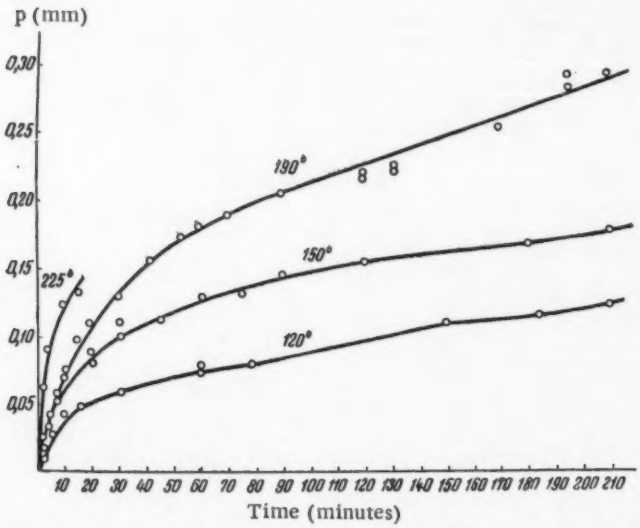

Fig. 4. Kinetic curves for the dehydration of isopropyl alcohol in a surface layer on zinc oxide.

The closeness of the figures in the last two columns indicates that the view that the decomposition of isopropyl alcohol proceeds mainly only in two parallel directions (dehydrogenation and dehydration) is correct.

Fig. 3 shows the growth of pressure when the reaction products are frozen out with liquid N_2, i.e., kinetic curves for the dehydrogenation of the alcohol. In order to obtain kinetic curves for the dehydration of the alcohol we doubled the ordinates of curves for the growth of pressure with freezing-out by means of liquid N_2 and subtracted then from the ordinates of curves for the growth of pressure with freezing-out by means of CO_2. The results of this operation are given in Fig. 4.

The kinetic curves for the dehydrogenation of isopropyl alcohol in the adsorbed layer on ZnS are given in Fig. 5, and the kinetic curves for dehydration in a surface layer on ZnS are given in Fig. 6, these being calculated

by subtraction of ordinates of curves for the growth fof pressure with freezing-out by means of solid propyl alcohol (−115°) from the ordinates of the curves in Fig. 5. Construction of curves from various kinetic equations showed that the experimental data fit best to the equation characteristic for an inhomogeneous surface:

$$q = at^{1/n},$$

in which q is the amount that has reacted, t is time, and a and n are constants. Fig. 7 shows kinetic curves corresponding to this equation for the dehydrogenation of isopropyl alcohol over ZnS in bilogarithmic coordinates (log q against log t).

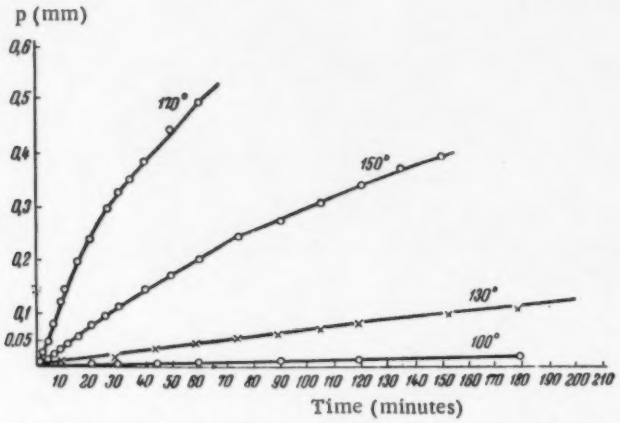

Fig. 5. Kinetic curves for the dehydrogenation of isopropyl alcohol in a surface layer on zinc oxide.

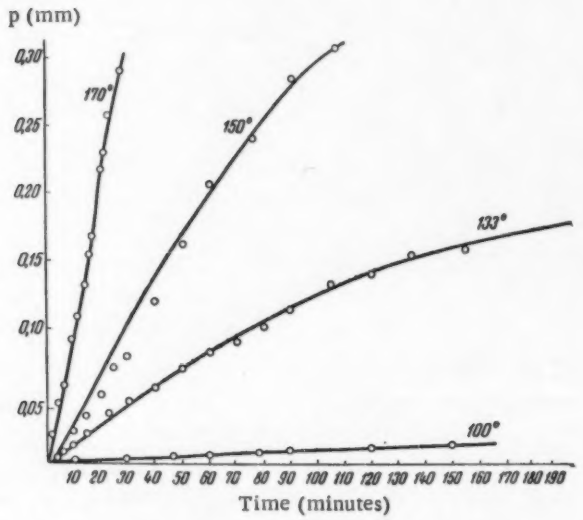

Fig. 6. Kinetic curves for the dehydration of isopropyl alcohol in a surface layer on zinc oxide.

The activation energy for reaction in the surface layer can be calculated from the formula:

$$E_q = R\frac{d\ln t_q}{d(1/T)}, \qquad (1)$$

in which t_q is the time required for the reaction of a definite amount q of adsorbed substance at temperature T, and E_q is the activation energy at the corresponding surface coverage [10]. Equation (1) is valid when the initial coverages are equal. In view of the low adsorption of the alcohol on the sample at high temperatures, it could not be measured on the McBain balance. Hence, for the determination of the adsorption we determined the total pressure of reaction products after desorption at high temperatures (350-400°), in an analogous manner to the procedure in Levin's experiments [10] on the decomposition of methanol. In the calculation of the coverage it was assumed that the area of a molecule of isopropyl alcohol [11] is 20 A^2 and that its decomposition leads to the formation of two new molecules which are desorbed into the gas phase. The resulting values of coverage were expressed in terms of the surface areas of ZnO and ZnS measured by adsorption of heptane. The values obtained are given in Table 3 and shown graphically in Fig. 8.

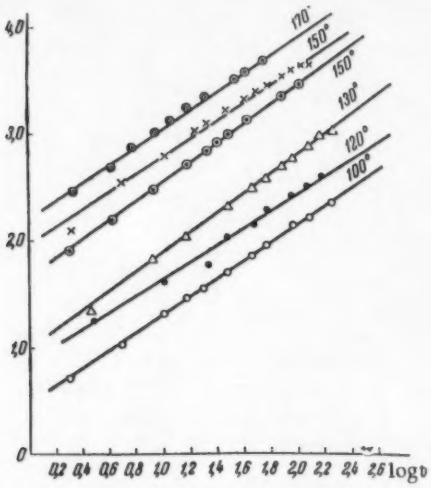

Fig. 7. Kinetic curves for the dehydrogenation of isopropyl alcohol in a surface layer on ZnS in bilogarithmic coordinates (log q against log t).

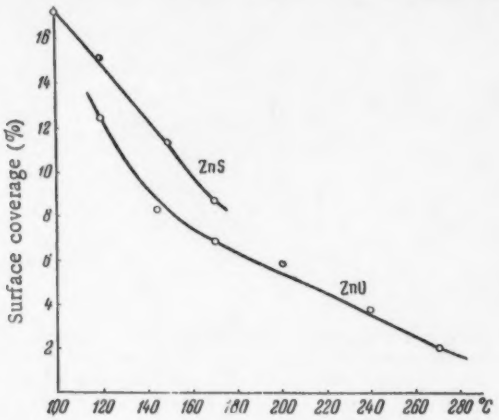

Fig. 8. Temperature-dependence of surface coverage in the adsorption of isopropyl alcohol on ZnO and ZnS.

TABLE 3

Surface Coverage of ZnO and ZnS in the Adsorption of Isopropyl Alcohol

Temperature (°C)	100	120	145	150	170	200	240	270
Surface coverage of ZnO (%)		12.5	8.3		6.9	5.9	3.8	2.1
Surface coverage of ZnS (%)	17.2	15.2		13.4	8.7			

It will be seen from Table 3 that the values of the adsorption of the alcohol per unit surface on ZnO and ZnS do not differ greatly, but fall sharply with rise in temperature. In our case, therefore, it is impossible to calculate E_q from Equation (1) for a wide range of temperatures, as Levin did [10]. For the tentative estimation of E by an analytical method we used Equation (1) only for two temperatures fairly close together (differing by 20-30°) on the assumption that in this case there would be little difference in the initial coverage. The value obtained for ZnO are given in Table 4, and those for ZnS in Table 5.

We carried out experiments also on the acid-base properties of zinc and cadmium sulfides. Table 6 gives the results on the adsorption and desorption of phenol and pyridine on the catalysts investigated.

TABLE 4

Activation Energy for the Decomposition of Isopropyl Alcohol in a Surface Layer on ZnO

Temperature (°C)	Coverage (%)	Value of E of dehydrogenation for different parts of the kinetic curves	Mean E of dehydrogenation (kcal/ mole)	Value of E of dehydration for different parts of the kinetic curves	Mean E of dehydration (kcal/ mole)
120-150	10	27; 27; 22	25	15; 17; 15	16
150-190	6	34; 28; 30; 28	30	15; 14; 12	14
190-225	4,5	47; 46; 45	46	12; 15	14

TABLE 5

Activation Energy for the Decomposition of Isopropyl Alcohol in a Surface Layer on ZnS

Temperature (°C)	Coverage (%)	Value of E of dehydrogenation for different parts of the kinetic curves	Mean E of dehydrogenation (kcal/ mole)	Value of E of dehydration for different parts of the kinetic curves	Mean E of dehydration (kcal/ mole)
100-130	16	19; 18; 18; 20; 15	18	22; 22; 21	22
130-150	14	30; 28; 31; 29	29	25; 23; 24; 25; 22; 21	23
150-170	11	40; 42	41	24; 25; 23	24

TABLE 6

Adsorption of Phenol and Pyridine on Sulfides (micromoles/ mg).

Catalyst	Specific surface (sq.m/ g)	Adsorption of phenol at 25°	Amount remaining after desorption at			Adsorption of pyridine at 25°	Amount remaining after desorption at	
			25°	100°	200°		25°	100°
ZnS*	108	3,4	2,9	0,2	0	4,7	—	—
ZnS	145	2,6	2,4	0,3	0	5,3	2,1	0,2
CdS	47	4,4	3,6	0,1	0	5,5	4,3	0
CdS*	71	4,4	3,7	0,4	0	5,6	2,1	—
$ZnS + ZnSO_4$*	101	5,0	4,1	1,9	0,7	6,0	1,7	0,5

DISCUSSION OF RESULTS

In most investigations in which parallel studies have been carried out on the oxides and sulfides of the same metals it has been found that the sulfides are better catalysts than the corresponding oxides. Thus, Lozovoi, Seniavin, and Vol'-Epshtein found that tungsten, vanadium and molybdenum sulfides are more active than the corresponding oxides in the hydrogenation of benzene and naphthalene [12].

According to Belen'kii and Sultanov [2], replacement of part of the ZnS and ZnO results in reduced catalytic activity for the dehydrogenation of ethylbenzene. In this review article, Griffith [13] states that, as a catalyst for destructive hydrogenation, MoS_2 is more active than MoO_2. These examples could be multiplied. An exception is found in the work of Steevens, Kee, and Trivich [14], who found the catalytic activity of oxides to be greater than that of the corresponding sulfides for a somewhat unusual catalytic reaction of photosynthesis of hydrogen peroxide. Dolgov, Karpinskii, and Silina [3], and also Krylov, Danchevskii, and Kobozev [4], found the catalytic activities of ZnO and ZnS to be approximately the same for the decomposition of methanol. It must be pointed out that in most of these investigations no surface-area measurements were carried out on the catalysts.

In accordance with the views on the mechanism of the decomposition of alcohols developed in the Catalysis Laboratory of the Institute of Physical Chemistry of the Academy of Sciences of the USSR [6, 15], the dehydrogenation

of alcohols is a process of the electronic type and should be catalyzed mainly by compounds of the transition elements, by semiconductors, and by metals. As regards the "semiconductor" properties of oxides and sulfides it is known [16] that, as we pass from the oxides of metals to the sulfides, the ionic contribution to the bond diminishes and the covalence contribution increases, so that the width of the forbidden zone diminishes. The mobility of the current carriers increases.

If we examine the acid-base properties of the sulfides that we have studied (Table 6) and compare them with the acid-base properties of the corresponding oxides [9], we find that the surfaces of ZnS and CdS have greater powers for the adsorption of bases and smaller powers for the adsorption of acids than the surfaces of ZnO and CdO. In the desorption of weak acid phenol, there is complete removal from the surfaces of ZnS and CdS at 200°, whereas this does not occur until 300-400° is reached in the case of the corresponding oxides. On the other hand, the weak base pyridine is more strongly bound to the surfaces of the sulfides. After desorption at 25° there remains 30-70% of adsorbed pyridine on the surfaces of ZnS and CdS, but less than 20% on the surfaces of ZnO and CdO. If the views concerning the importance of the acidic properties of the catalyst for dehydration are correct, then replacement of oxides by sulfides should increase catalytic activity with respect to the dehydration of alcohols.

Attempts to explain the change in catalytic properties as we pass from oxides to sulfides with the aid of multiplet concepts were not successful. Thus, Rubinshtein [17], in order to explain the above-mentioned results of Griffith on the catalytic activities of MoO_2 and MoS_2 in the hydrogenation of ethylene, was forced to reject the two-point scheme for the adsorption of the olefin and assume a special mechanism with the simultaneous participation of six atoms of catalyst, this being the only way in which the experimental data could be given a theoretical explanation.

The rate constants for reaction over ZnS and CdS are higher than those for reaction over ZnO and CdO [6, 7]. Thus, over ZnS the lowest temperature at which we could detect the dehydrogenation of isopropyl alcohol under our flow conditions (in an amount corresponding to 1-2% decomposition) was 202°, and over CdS it was 134°; over ZnO and CdO the corresponding temperatures were 240° and 190° respectively, though the surface areas of the oxides were greater than those of the corresponding sulfides. Nevertheless, the activation energies for dehydrogenation over various samples of sulfides were close in value to those for dehydrogenation over the oxides. Over various samples of ZnO the activation energy for dehydrogenation ranged from 12,000 to 18,000 cal/mole; over ZnS it ranged from 15,500 to 20,500 cal/mole (see Table 1), i.e., was somewhat higher. Over CdO the activation energy for dehydrogenation was 10,000-16,000 cal/mole and over CdS it had similar values (11,000-17,000 cal/mole). Over PbS activation energies for dehydrogenation were again somewhat higher than over PbO. Addition of sulfate had little effect on the activation energy, while considerably lowering the total activity.

The results of the investigation of the decomposition of isopropyl alcohol in a surface layer support, in general, the conclusions reached from the experiments under flow conditions. The activation energy for the dehydrogenation of isopropyl alcohol in an adsorption layer on ZnO depends greatly on the coverage and varies over the range 25-46 kcal/mole; in an adsorption layer on ZnS it ranges from 19 to 42 kcal/mole. The kinetic equation for the dehydrogenation in an adsorption layer corresponds to a heterogeneous surface with an exponential distribution with respect to activation energies. The activity of ZnS for reaction in the layer is higher than that of ZnO, as in the case of reaction under flow conditions. We must point out also some differences. Whereas dehydrogenation predominates over ZnO and over ZnS under flow conditions, when decomposition occurs in a surface layer on ZnO dehydration predominates and over ZnS dehydrogenation and dehydration occur to comparable extents. These facts also support the view that activity is greatly dependent on surface coverage (inhomogeneity or repulsion).

The great dependence of catalytic activity on coverage, the increase in catalytic activity and hydrogenating power as we pass from oxides to sulfides, the results of a comparison of these changes with changes in semiconductor properties (size of forbidden zone, mobility and number of current carriers), the effect of additions, and other facts support the view that the catalytic properties of sulfides and oxides are associated with their chracteristics as semiconductors. This matter will be examined in greater detail in a future publication, in which the results of the present work will be compared with results on the catalytic properties of selenides and tellurides.

According to our results, activation energies for dehydration in an adsorption layer have extremely low values (14-16 kcal/mole for ZnO and 23-24 kcal/mole for ZnS) with change very little with change in surface coverage, under the given conditions. We must point out, however, that in the calculation of activation energies for dehydration in the layer considerable errors can arise in the subtraction of ordinates, which is carried out for

the construction of the dehydration kinetic curves (Figures 4 and 6). Addition of sulfate to sulfide increased its dehydrating power, as in the case of the oxide. The addition scarcely affected the activation energy for dehydration.

The activity of CdS is higher than that of ZnS, but the activation energy for dehydrogenation is lower, i.e., in this case the rules found for oxides (increase in catalytic activity with increase in the atomic weight of the metal) are confirmed also for sulfides. Radiochemical and x-ray results [8] indicate that pure ZnS and CdS are stable under the conditions of the decomposition of isopropyl alcohol.

SUMMARY

1. A study was made of the catalytic decomposition of isopropyl alcohol in a flow system at atmospheric pressure at temperatures ranging from 190° to 392° over Zn, Cd, Hg, Pb, and Bi sulfides, over ZnS with added $ZnSO_4$, over CdS with added $CdSO_4$, and over Pb and Bi oxides.

2. Apart from PbS, all the sulfides studied were predominantly dehydrogenation catalysts. Under the experimental conditions dehydration proceeded only on a small scale. Passage of air through the catalyst and addition of sulfate increased the extent to which dehydration of isopropyl alcohol occurred.

3. The catalytic activities of Zn and Cd sulfides are greater than those of ZnO and CdO. The activation energy for dehydrogenation is lower over CdS than over ZnS. Change in the method of preparing the sulfide leads to change in its catalytic properties.

4. Under the conditions of decomposition of isopropyl alcohol in an adsorption layer, the activity of ZnS is greater than that of ZnO. In an adsorption layer on ZnO and on ZnS the activation energy for dehydration is lower than the activation energy for dehydrogenation. The activation energy for dehydrogenation in an adsorption layer increases as surface coverage increases.

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Received January 8, 1957

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NEW METHOD OF DETERMINING RATE CONSTANTS OF ELEMENTARY REACTIONS OF ATOMS AND RADICALS

L. I. Avramenko, R. V. Kolesnikova, and L. M. Postnikov

The main obstacle to the study of the kinetics of elementary reactions of atoms and radicals lies in the experimental difficulties encountered in the quantitative measurement of concentrations of short-lived particles. The scantiness of the information available on the rate constants of reactions of atoms and radicals is associated with the absence of simple and reliable methods of measuring these constants. Rate constants of reactions of, for example, oxygen atoms, cannot be determined by known methods [1-11]. The present authors have developed a new method of determining absolute rate constants of reactions of atomic oxygen, and they suggest its use as a general method of obtaining absolute rate constants of the gas-phase reactions of other atoms and radicals.

In this method it is usually possible to avoid difficulties associated with the measurement of absolute concentrations of atoms and radicals. For the sake of simplicity, in our exposition of the essence of the method we shall take the reactions of atomic oxygen with various molecules as our model. Let us examine the phenomena occurring in the vessel shown diagrammatically in the figure. Oxygen atoms, together with the molecular oxygen or water vapor from which these atoms have been generated under the action of the electric discharge [12], move with constant velocity $\underline{w}$ through this vessel. Along the length of the vessel there will be a certain distribution of atom concentrations, both when a combustible reactant ("fuel") is fed into the vessel, and also when it is not.

When no fuel is fed into the vessel, the oxygen atoms will be consumed in recombination (in the bulk phase and at the walls) and in reaction with gases passing from the discharge (H_2O, H_2, or O_2). When fuel is admitted, apart from these reactions there will be reactions between oxygen atoms and the fuel and still further reactions between oxygen atoms and the primary reaction products. Let us examine the second case: fuel is admitted to the vessel, but flameless reaction with oxygen atoms occurs. All processes occurring under the conditions of our experiments can be represented by the following general scheme:

$O + A \xrightarrow{k_1}$	B	k_1'	Primary products
	$B_1 + R_1$	k_1''	
	$B_2 + R_2$	k_1'''	
	. . . .		
	$B_n + R_n$	k_1^{n+1}	
	$R_1' + R_2'$	k_1^{n+2}	
$R_n + O_2 \xrightarrow{k_2}$	$C + R_3'$	k_2'	Secondary products
$n = 1, 2, 3, \ldots$	ROO	k_2''	
$O + B_n \xrightarrow{(k_4)_n}$	$(D)_n$	$(k_4')_n$	Quadratic products
$n = 1, 2, 3, \ldots$	$(D_1)_n + R_4'$	$(k_4'')_n$	
$O + C \xrightarrow{k_5}$	D_5		
$O + D_n \xrightarrow{(k_3)_n}$	$(F)_n$	k_3'	Cubic products
	$(F_1)_n + R_5'$	k_3''	
$O + M \xrightarrow{k_0'}$	Linear termination in bulk phase		

$$O + \text{wall} \xrightarrow{k_0''} \text{Linear termination on walls}$$

$$O + O + M \xrightarrow{k_0'''} O_2 + M \quad \text{Quadratic termination}$$

In this scheme A is the original combustible reactant [fuel]; O is atomic oxygen; B, B_1, . . . B_n are primary stable reaction products; R, R_1, . . . R_n are radicals or atoms; k_1, k_2, . . . k_n are over-all rate constants; k_1', k_1'', . . . k_1^n are rate constants of the corresponding elementary reactions; C comprises secondary reaction products; $(D)_n$, $(D_1)_n$, etc. are quadratic reaction products; $(F)_n$, $(F_1)_n$, etc. are cubic reaction products; ROO is a peroxide radical; M is a stable molecule.

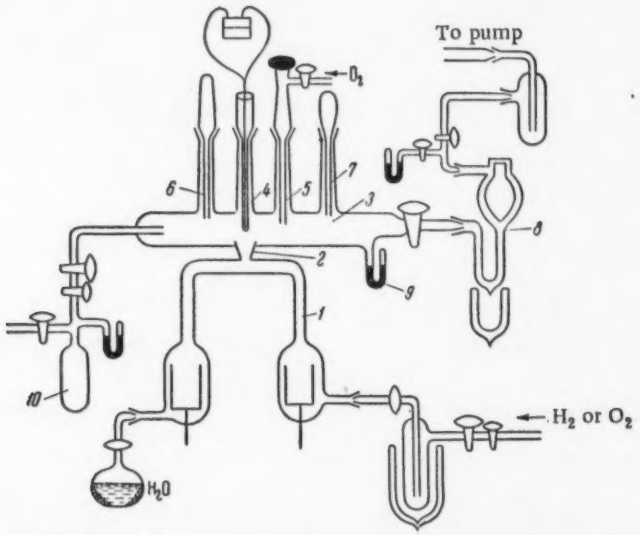

Diagram of apparatus: 1) discharge tube; 2) jet; 3) reaction vessel; 4) thermocouple; 5, 6, 7) inlets for additions of O_2; 8) detachable trap; 9) manometer; 10) calibrated flask.

Reactions of the original substance A with radicals formed in the reaction are neglected in this scheme, and the kinetic equation for the original fuel will therefore have the form:

$$\frac{d(A)}{dt} = -k_1(A)(O). \tag{1}$$

The kinetic equation for the rate of disappearance of atomic oxygen under such experimental conditions can be written in the form:

$$-\frac{d(O)}{dt} = k_1(A)(O) + \sum k_4^n(O)(B_n) + \sum k_3^m(O)(D_m) + \\ + k_5(O)(C) + k_0(O) + k_0'''(O)^2(M), \\ n = 1, 2, 3, \ldots \quad m = 1, 2, 3 \ldots \tag{2}$$

in which k_0 is the effective constant for linear termination of the life of oxygen atoms in absence of A and its reaction products; k_0''' is the constant of quadratic recombination. Dividing Equation (2) by Equation (1), we obtain:

$$\frac{d(O)}{d(A)} = 1 + \frac{\sum_n k_4^n(B_n)}{k_1(A)} + \frac{\sum_m k_3^m(D_m)}{k_1(A)} + \frac{k_5(C)}{k_1(A)} + \frac{k_0}{k_1(A)} + \frac{k_0'''(O)(M)}{k_1(A)}. \tag{3}$$

In order to integrate Equation (3) it is necessary to know the relations of B_n, D_m, and C to A. We have deduced these relations previously [13] in an exposition of the method of determining the sequence of elementary reactions of atoms and radicals. In accordance with this method the values of B_n, D_m, and C are expressed as follows in terms of A and A_0:

$$B_n = \frac{k_1^{(1+n)}}{k_1 - k_4^{(n)}} \left[A_0^{1-\frac{k_4^n}{k_1}} A^{\frac{k_4^n}{k_1}} - A \right] \tag{4}$$

$$D_m = \frac{k_1^{1+m} \cdot k_4^{1+m}}{k_1 - k_4^m} A_0 \left\{ \left(\frac{1}{k_4^m - k_3^m} - \frac{1}{k_1 - k_3^m} \right) A_0^{-\frac{k_3^m}{k_1}} A^{\frac{k_3^m}{k_1}} - \right.$$

$$\left. - \left[\frac{A_0^{-\frac{k_4^m}{k_1}} A^{\frac{k_4^m}{k_1}}}{k_4^m - k_3^m} - \frac{A}{A_0 (k_1 - k_3^m)} \right] \right\} \tag{5}$$

$$C = \frac{k_1 \cdot k_2}{k_1 - k_0} \left[A_0^{1-\frac{k_2}{k_1}} A^{\frac{k_2}{k_1}} - A \right] \tag{6}$$

By substitution of the values of B_n, D_m, and C we obtain the differential equation in the form:

$$d(O) = d(A) + \frac{d(A)}{k_1 (A)} f(A, A_0) + \frac{k_0}{k_1} \frac{d(A)}{(A)} + \frac{k_0''' (O) M}{k_1} \cdot \frac{d(A)}{(A)} . \tag{7}$$

Integration of this differential equation under the limiting conditions of $A = A_0$, $(O) = (O)_0$ and $A = A_k$, $(O) = O$ gives:

$$\alpha^{\frac{k_0''' M}{k_1}} = 1 - \frac{\frac{(O)_0}{A_0} + a(\alpha - 1) + b\left(\alpha^{\frac{k_1}{k_1}} - 1\right) + c\left(\alpha^{\frac{k_2}{k_1}} - 1\right)}{\frac{(O)_0}{A_0} + \frac{k_0}{k_0''' M A_0} - (a + b + c)} , \tag{8}$$

in which

$$\alpha = \frac{A_k}{A_0} = 1 - \frac{\sum_n (B_k)_n + \sum_m (D_k)_m + \sum_l (F_k)_l}{A_0} ;$$

$$a = \frac{k_1}{k_1 - k_0''' M} + \frac{k_1 k_4}{(k_4 - k_1)(k_1 - k_0''' M)} - \frac{k_1 k_3 k_4}{(k_4 - k_1)(k_1 - k_3)(k_1 - k_0''' M)} ;$$

$$b = \frac{k_1 k_3 k_4}{(k_4 - k_1)(k_4 - k_3)(k_4 - k_0''' M)} - \frac{k_1 k_4}{(k_4 - k_1)(k_4 - k_0''' M)} ;$$

$$c = \frac{k_1 k_3 k_4}{(k_4 - k_1)(k_1 - k_3)(k_3 - k_0''' M)} - \frac{k_1 k_3 k_4}{(k_4 - k_1)(k_4 - k_3)(k_3 - k_0''' M)} ;$$

α is always less then 1, so that if we select sufficiently high values of A_0 conditions can always be realized under which we may, without appreciable error, limit ourselves to the second terms of the expansions of $\alpha^{\frac{k_0''' M}{k_1}}$, $\alpha^{\frac{k_4}{k_1}}$ and $\alpha^{\frac{k_3}{k_1}}$ into series.

Expanding into series in this way and taking only the first two terms, we obtain from Equation (8):

$$\frac{k_0''' M}{k_1} \sum = \frac{\frac{(O)_0}{(A)_0} - \left(a + \frac{k_4}{k_1} b + \frac{k_3}{k_1} c\right) \sum}{\frac{(O)_0}{A_0} + \frac{k_0}{k_0''' M} - (a + b + c)}, \tag{9}$$

in which

$$\sum = \sum_n (B_k)_n + \sum_m (D_k)_m + \sum_l (F_k)_l.$$

After further simple algebraic transformations and substitutions of the values of a, b and c, expressed in terms of the constants k_1, k_4, k_3, and $k_0'''M$, from Equation (9), we obtain:

$$\frac{1}{\Sigma} = \frac{1}{(O)_0} + \frac{k_0 + k_0''' M (O)_0}{k_1 (O)_0} \cdot \frac{1}{A_0} \tag{10}$$

Equation (10) is linear. By measuring experimentally the values of Σ at various values of A_0 and constructing the graph of $\frac{1}{\Sigma}$ against $\frac{1}{A_0}$, we may from the slope of the graph, obtain

$$\tan \beta = \frac{k_0 + k_0''' M (O)_0}{k_1 (O)_0}. \tag{11}$$

From the intercept on the axis of ordinates we may obtain the value of $\frac{1}{(O)_0}$. From the graph in this way we obtain the absolute value of the over-all constant k_1 at the given temperature if, of course, the values of k_0 and $k_0'''M$ are known under the given experimental conditions. Having determined $\tan \beta$ at various temperatures, we may calculate the temperature-dependence of the constant k_1 and therefore also the activation energy and the preexponential factor.

The above considerations apply to the determination of over-all rate constants of primary reactions of atoms or radicals. We often have to deal with reactions in which there is only one primary product. In such cases everything is simplified in that we no longer deal with a sum of constants, but with the single constant of an elementary reaction. Still more frequently, however, we have to deal with reactions in which there are several primary elementary reactions, so that not only the over-all rate constant of the primary reactions is of interest, but also the rate constants of the individual elementary reactions. In order to solve this question we may take the following considerations as our starting point: the over-all rate constant of the primary reactions, as can be seen from the general reaction scheme and from the definition, is the sum of all the constants of the primary elementary reactions

$$k_1 = k_1' + k_1'' + k_1''' \text{ etc.}$$

In order to determine the values of k_1', k_1'', k_1''' when k_1 is known, it is necessary to know the ratios $\frac{k_1'}{k_1}$, $\frac{k_1''}{k_1}$ and $\frac{k_1'''}{k_1}$. These ratios can be determined if in some way we can determine the rates of conversion into the respective primary products and the over-all rate of conversion of the original substance.

The rate of conversion into a given product can be written in the form:

$$\int_0^l S k_1' (O)(A)\, dl = (B_k)' WS.$$

$$\int_0^l S k_1'' (O)(A)\, dl = (B_k)'' WS;$$

$$\int_0^l Sk_1''' (O)(A)\,dl = (B_k)''' WS \text{ etc.}$$

The over-all rate of conversion of the original substance A can be expressed as

$$\int_0^l Sk_1 (O)(A)\,dl = WS\left[\sum_n (B_k)_n + \sum_m (D_k)_m + \sum_l (F_k)_l\right] = WS\sum.$$

Therefore

$$\frac{Sk_1' \int_0^l (O)(A)\,dl}{Sk_1 \int_0^l (O)(A)\,dl} = \frac{(B_k)'}{\Sigma} = \frac{k_1'}{k_1}$$

$$\frac{(B_k)''}{\Sigma} = \frac{k_1''}{k_1} \text{ and } \frac{(B_k)'''}{\Sigma} = \frac{k_1'''}{k_1}.$$

The over-all rate of conversion of the original substance can be determined either from the consumption of the substance in unit time, or from the sum of the rates of formation of all the reaction products formed. The rate of conversion into a given primary product can be determined from the limiting rate of accumulation of that product, if it is stable, or from the limiting rate of accumulation of a secondary product, if the primary product is a radical. We may recall that, according to conclusions based on the sequence method [13], at high concentrations of the original substance A_0 a limiting rate of accumulation of primary and secondary products is established, but the rate of accumulation of quadratic products tends to zero. Hence, by measuring the rate of accumulation of an individual primary product when this has attained its limit we exclude errors in the determination associated with the consumption of the primary product in quadratic and cubic reactions.

In this way the rate constant of an individual elementary reaction can be determined from the equation:

$$k_1' = k_1 \frac{(B_k)'}{\Sigma}. \tag{12}$$

Substituting the value of Σ given by this equation in Equation (10), we obtain:

$$\frac{1}{(B_k)'} = \frac{k_1}{k_1' (O)_0} + \frac{k_0 + k_0''' M (O)_0}{k_1 (O)_0} \cdot \frac{k_1}{k_1' (A_0)}. \tag{13}$$

Equation (13) shows that for the determination of the over-all rate constant for the reaction of atomic oxygen k_1 there is no need to measure all the primary reaction products or the sum of all reaction products, it being sufficient t to measure the rate of accumulation of one of the primary reaction products in order to determine the over-all constant k_1 (not the individual constant). Naturally, as primary product we should select the one which can be most readily subjected to measurement and which give rise to no doubts concerning its primary origin. A similar result is obtained if measurements are made on the rate of accumulation of several primary products simultaneously, rather than of only one.

The only complication arising in the case in which $k_0 \simeq k_0'''M(O)_0$ consists in the necessity for the supplementary determination of the value of $(O)_0$. Two special cases arise from Equation (13), one of which enables us to determine the over-all constant k_1, and the other the individual constant k_1'.

In the case in which the rate of linear recombination predominates over quadratic, i.e., when $k_0 \gg k_0'''M(O)_0$, we obtain from Equation (13):

$$\frac{1}{(B_k)'} = \frac{k_1}{k_1' (O)_0} + \frac{k_0}{k_1 (O)_0} \cdot \frac{k_1}{k_1' A_0} \tag{14}$$

Hence, from Equation (14) (from the slope and intercept on the axis of ordinates) we obtain the over-all constant k_1 without measuring $(O)_0$.

In the case in which the rate of quadratic recombination of oxygen atoms predominates over linear recombination, i.e., when $k_0 \ll k_0'''M(O)_0$, we obtain:

$$\frac{1}{(B_k)'} = \frac{k_1}{k_1'(O)_0} + \frac{k_0'''M}{k_1'A_0}. \qquad (15)$$

From Equation (15) (without measuring the sum of all the products and without measuring $(O)_0$)we obtain the value of the individual constant k_1' (from the slope of the straight line).

Hence, by the use of the proposed method of measurement we may determine both the over-all rate constant of the reaction of oxygen atoms and also the constants of individual primary elementary reactions. We must point out, however, that in using this method we must not forget the limitations to its applicability. The point is that all our conclusions are valid when A_0 (initial concentration of the original substance) is large in comparison to $(O)_0$ (initial concentration of oxygen atoms), when the formation of quadratic and cubic products no longer plays an important part, but at the same time A_0 must not be too large, for at some value of A_0 further increase in B_k' ceases. There need be no surprise , therefore, if a straight line is not obtained experimentally for all values of A_0. The absence of a straight line for a particular primary product will indicate that our method is not applicable over a wide range of values of A_0. However, it must be supposed that there will always be a range of values of A_0 for which, at sufficiently high values of A_0 we may recognize a linear section from which we may determine the constants. Experiment will show whether this statement is true.

All the above considerations remain valid when it is necessary to determine rate constants of reactions of any other atoms or radicals. For other atoms and radicals there will be, of course, other concrete reaction schemes. It is obvious also that for each atom or radical its constants k_0 and k''' must be measured under the conditions of the particular experiments, but the method of investigation may remain unchanged in almost all details and will give both over-all constants and individual rate constants of the elementary reactions. By way of illustration we have examined such a scheme for the reaction of methyl radicals with an oxygen molecule:

$$CH_3 + O_2 \xrightarrow{k_1} CH_3OO \quad k_1$$

$$CH_3OO \xrightarrow{+CH_3COCH_3} CH_3OOH + CH_3COCH_2 \quad k_2$$

$$CH_3OO \xrightarrow{k_3} H_2O + HCO \quad k_3$$

$$CH_3 + CH_3COCH_3 \xrightarrow{k_0''} CH_4 + CH_3COCH_2 \quad k_0''$$

$$CH_3 + CH_3 \xrightarrow{k_0'''} C_2H_6 \quad k_0'''$$

$$CH_3 \xrightarrow{\text{wall}} \text{termination} \quad k_0'$$

On the basis of this reaction scheme for the CH_3 radical (which can be prepared by the thermal dissociation of acetone) with application of the method of measurement and inference given above, we may obtain a relation between the rate of accumulation of hydroperoxide and the initial concentration $(O_2)_0$ in the form:

$$\frac{1}{(CH_3OOH)_k} = \frac{1 + \frac{k_3}{k_2(CH_3COCH_3)}}{(CH_3)_0} + \frac{k_0 + k_0'''(CH_3)_0}{k_1(O_2)_0(CH_3)_0}\left(1 + \frac{k_3}{k_2(CH_3COCH_3)}\right). \qquad (16)$$

Equation (16), like Equation (13), is represented by a straight line, from the slope and intercept of which we may obtain the over-all rate constant of the elementary reaction $CH_3 + O_2 \xrightarrow{k_1} CH_3OO$ if k_0, k_0''' and $(CH_3)_0$ are known.

in the general case, or if only k_0 or k_0''' $(CH_3)_0$ is known, in special cases.

We have here considered reactions of a diradical (oxygen atom) and of a monoradical (CH_3). The identity of the conclusions at which we arrive in these two cases leads us to believe that our method may be applicable to any other types of radicals and atoms. With the aid of the above-described method we have obtained rate constants of the elementary reactions of oxygen atoms with molecules such as Co, CH_4, and CH_3OH, and we have obtained also rate constants for the reactions of CH_3 and C_2H_5 radicals with the oxygen molecule. These results will be described in detail in a future publication.

In conclusion the authors express their thanks to N. N. Semenov and V. N. Kondrat'ev for valuable advice.

SUMMARY

A new method is proposed for the determination of absolute values of the rate constants of elementary reactions of atoms and radicals with molecules in the gas phase.

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Received January 21, 1957

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** Original Russian pagination. See C. B. Translation.

CAPILLARY CONDENSATION OF VAPOR IN HIGHLY DISPERSED SYSTEMS

COMMUNICATION 2. APPRAISAL OF SOME APPROXIMATE CALCULATIONS OF VOLUMES OF CAPILLARY CONDENSATE

L. V. Radushkevich

In the first communication [1] we calculated volumes of capillary condensate near the point of contact of two identical spherical particles. In this calculation we took account of the requirement of thermodynamic equilibrium between vapor and liquid situated between the two spheres in contact. Also, it was assumed that the surfaces of the particles are completely wetted with the liquid, for at the vapor pressures at which the start of capillary condensation may be expected the surfaces of the particles are already covered with an adsorbed multimolecular film that ensures complete wetting under all conditions. The effect of the weight of condensed substance on the profile of the meniscus can be neglected entirely because of the negligible amount of liquid at the point of contact. All these considerations enable us to assert that our calculations are extremely accurate and have a sound physical basis. The initial calculations are somewhat cumbersome, but they provide a set of tables which can readily be applied in the final calculations. Nevertheless, an approximate solution of the problem would be of some interest. In connection with various practical requirements, various authors have given schemes for the approximate calculation of volumes of liquid near the point of contact between two spheres of equal radius. Thus, in Leibenzon's monograph [2] calculations were made of the volume of petroleum held near the points of contact of grains of sand in connection with problems of filtration of petroleum through beds of earth. Higuti and Utsugi [3], using an approximate method, found the volume of liquid in an analogous case in connection with the interpretation of adsorption isotherms of vapors. In a paper at a Faraday Society Discussion, Davies [4] also gave approximate calculations of the same quantity in an examination of the question of contact angles and the part played by gravity in the drainage of water in sands. For the determination of the retained water in granular foodstuffs, similar approximate calculations were carried out by Lykov [5]. The necessity for similar calculations is met also in various fields of technology [6].

In all these investigations, and also in other cases discussed below, the main simplifying assumption is that the profile of the meniscus of liquid between the particles in contact is an arc of a circle. This assumption does indeed simplity the calculations, though, strictly speaking, the requirement of constant curvature at all points of the liquid surface at equilibrium means that at $p/p_s < 1$ the profile is an arc of a trochoid, which passes into a section of a catenary at $p/p_s = 1$.

It is easy to show that, whatever simplified model we may take for a system of two spheres in contact, if we assume that the profile of the meniscus is an arc of a circle, on the basis of geometric construction the required volume will be given by the expression:

$$V_{approx} = 2\pi R^3 \cdot \alpha^2 \left(1 - \sqrt{2\alpha + \alpha^2} \cdot \arcsin \frac{1}{1+\alpha}\right), \quad (1)$$

in which V_{approx} is the volume of liquid between the spheres, R is the radius of a sphere, and $\alpha = r/R$, the ratio of the radii of meniscus and sphere. If, for convenience, we introduce the function

$$Y(\alpha) = \alpha^2 \left(1 - \sqrt{2\alpha + \alpha^2} \cdot \arcsin \frac{1}{1+\alpha}\right), \quad (2)$$

then

$$V_{approx} = 2\pi R^3 \cdot Y(\alpha). \tag{1'}$$

In these equations α depends on the relative vapor pressure p/p_s, and the character of the relationship is determined by the assumption made about the curvature of the liquid surface. In calculations it is simpler to introduce a function of α which we call the model function $\Psi(\alpha)$, from which we find α at a given value of p/p_s. In the further treatment we shall always assume complete wetting of the surface of the particles.

In the general case the curvature of the liquid surface between the spheres can be expressed by Kelvin's equation:

$$K = 1/r_1 + 1/r_2 = 2/C, \tag{3}$$

in which r_1 is the radius of the concave profile, r_2 is the radius of the inverse curvature, and C is given by

$$C = \frac{2\sigma v_0}{R_0 T \ln p_s/p}. \tag{4}$$

Corresponding to simplified concepts of the concave meniscus of liquid near the point of contact, at least five models are possible, and these give values of r_1 and r_2 and the associated Kelvin radius C of Equation (4).

Model A. Let us suppose that $r_1 = r_2 = r$. Then it follows from Equation (3) that

$$r = C = \frac{2\sigma v_0}{R_0 T \ln p_s/p}.$$

Therefore, $r/R = \alpha = C/R$, i.e., the model function has its simplest form:

$$\Psi_A(\alpha) \equiv \alpha = C/R. \tag{5}$$

Taking any value of p/p_s we find C from Equation (4) and therefore α; from (2) we then obtain the relative volume $Y(\alpha)$, and from (1) we obtain the value of the volume V.

This model has been used by Japanese workers [3]. Here, the meniscus near the point of contact is identified with the ciruclar meniscus in a cylindrical capillary.

Model B. At low relative pressures or with spherical particles of large size we may suppose that the internal curvature of the surface is much less than the external curvature, and in the limit we may assume approximately that $r_2 = \infty$. It then follows from (3) that

$$1/r_1 = 2/C.$$

This assumption is made in a paper by Chmutov [7]. Thus $\alpha = C/2R$, so that

$$\Psi_B(\alpha) \equiv \alpha = C/2R. \tag{6}$$

Model C. In his calculations Davies [4] assumes that at all points of the liquid layer the internal radius of curvature is equal to the minimum radius of the neck around the point of contact. Taking account of the different signs of r_1 and r_2, we have $r_2 = -r_{min}$ and

$$1/r - 1/r_{min} = 2/C.$$

From geometric construction it follows that $r_{min} = R(\sqrt{2\alpha + \alpha^2} - \alpha)$. . Hence, in the present case

$$\Psi_c(\alpha) \equiv \frac{1}{\alpha} - \frac{1}{\sqrt{2\alpha + \alpha^2} - \alpha} = 2R/C. \tag{7}$$

Model D. The internal radius of curvature of a liquid figure of rotation varies from r_{min} to R, and this gives us reason to suppose that a model in which the arithmetic mean of these radii is taken as the mean internal radius

of curvature should correspond somewhat better to the exact calculation than Model C; we therefore assume that

$$\bar{r} = \frac{r_{min} + R}{2}$$

and from geometric construction we obtain:

$$\bar{r} = R\,\frac{\sqrt{2\alpha + \alpha^2} - \alpha + 1}{2},$$

whence

$$\Psi_D(\alpha) \equiv \frac{1}{\alpha} - \frac{2}{\sqrt{2\alpha + \alpha^2} - \alpha + 1} = 2R/C. \tag{8}$$

Model E. It is possible that the introduction of the mean internal curvature will give results corresponding still more closely to exact calculation, so we may assume that

$$\bar{K} = \frac{K_{min} + K_{max}}{2}.$$

In this case the mean radius $\bar{r}_k$ is calculated from the relationship

$$\frac{1}{\bar{r}_k} = \frac{1}{R} \cdot \frac{1 + (\sqrt{2\alpha + \alpha^2} - \alpha)^{-1}}{2}.$$

Hence,

$$\Psi_E(\alpha) \equiv \frac{1}{\alpha} - \frac{1}{2}\left(1 + \frac{1}{\sqrt{2\alpha + \alpha^2} - \alpha}\right) = 2R/C. \tag{9}$$

It is easy to see that all five model functions are unified if we introduce a parameter $\underline{b} = 2R/C$. From Equations (5)-(9) we then find:

$$\left.\begin{aligned}
&\varphi_A(\alpha) \equiv 2/\alpha = b \\
&\varphi_B(\alpha) \equiv 1/\alpha = b \\
&\varphi_C(\alpha) \equiv 1/\alpha - \frac{1}{\sqrt{2\alpha + \alpha^2} - \alpha} = b \\
&\varphi_D(\alpha) \equiv 1/\alpha - \frac{2}{\sqrt{2\alpha + \alpha^2} - \alpha + 1} = b \\
&\varphi_E(\alpha) \equiv 1/\alpha - {}^1/_2[1 + (\sqrt{2\alpha + \alpha^2} - \alpha)^{-1}] = b
\end{aligned}\right\} \tag{10}$$

For a given sorbate and sphere radius the parameter $\underline{b}$ is readily calculated for various values of p/p_s. In the further treatment we shall confine ourselves to very small radii of spherical particles (R in the range 10^{-6}-10^{-4} cm). Comparison between approximate calculations and exact were made for the case of benzene at 20°, for which

$$C = 0{,}917 \cdot 10^{-7}\,(\lg p_s/p)^{-1} \text{ cm}$$

The approximated values of the volumes can be found most simply as follows. We first calculate values of $\underline{b}$ for benzene for various values of p/p_s in the range 0.5-1.0, and then from Equations (10), by direct calculation and graphically, we find the corresponding values of α for all five models. From these values of α we calculate the realtive volumes $Y(\alpha)$ with the aid of Equation (2).* In the comparison of the approximate volumes V_{approx}

*In the calculations we used Peters' Six-figure Tables of Trigonometric Functions (Geodesy Press, Moscow, 1941) and Barlow's Tables (Foreign Lit. Press, Moscow, 1950). The calculations were carried out on an arithmometer.

with the exact values V_{exact} we made use of the ratio

$$\epsilon = V_{approx} / V_{exact}$$

in which the numerator is given by Equation (1'),

$$V_{approx} = 2\pi R^3 \cdot Y(\alpha),$$

whereas V_{exact} is found from the equation

$$V_{exact} = {}^2/_3 \pi R^3 \cdot U = 2\pi R^3 \cdot V,$$

in which U is the value of the relative volume found by us in the first communication from exact theory [1]. Hence

$$\varepsilon = Y(\alpha)/V,$$

in which V = U/3.

The tables give values of ϵ for particle radii of $1 \cdot 10^{-6}$ and $1 \cdot 10^{-5}$ cm at various relative pressures together with the corresponding values of V. Analogous results were obtained for spheres of radii $5 \cdot 10^{-5}$ and $1 \cdot 10^{-4}$ cm, but for the sake of brevity we do not give these.

TABLE

p/p_s	A	B	C	D	E	V
			$R = 1 \cdot 10^{-6}$ cm			
	ε	ε	ε	ε	ε	
0,5	4,21	1,57	0,918	1,17	1,109	$59 \cdot 10^{-4}$
0,6	4,27	1,69	0,940	1 15	1,108	$86 \cdot 10^{-4}$
0,7	4,18	1,80	0,903	1,13	1,070	$132,8 \cdot 10^{-4}$
0,8	4,05	1,97	0,834	1,07	1,007	$219,0 \cdot 10^{-4}$
0,85	3,93	2,09	0,801	1,02	0,964	$293,3 \cdot 10^{-4}$
0,90	3,93	2,26	0,776	0,976	0,932	$413,3 \cdot 10^{-4}$
0 95	3,94	2,84	0,779	0,968	0,941	$556,7 \cdot 10^{-4}$
			$R = 1 \cdot 10^{-5}$ cm			
0,5	2,67	0,769	0,605	0,747	0,700	$2,33 \cdot 10^{-4}$
0,6	3,21	0,927	0,749	0,871	0,808	$3,33 \cdot 10^{-4}$
0,7	3,70	1,096	0,833	1,011	0,936	$5,38 \cdot 10^{-4}$
0,8	4,08	1,270	0,943	1,133	1,047	$10,67 \cdot 10^{-4}$
0,85	4,203	1,352	0,932	1,193	1,080	$17,25 \cdot 10^{-4}$
0,90	4,22	1,450	0,931	1,167	1,085	$33,00 \cdot 10^{-4}$
0,95	4,28	1,696	0,942	1,157	1,100	$85,67 \cdot 10^{-4}$

Analysis of the results leads to the conclusion that all the schemes of approximation, with the exception of that based on Model A, give the correct order of magnitude of the volumes of capillary condensate. The departures from the exact values, however, are considerable in the ranges of sphere dimensions and relative pressures that interest us. It is important to note that the discrepancies show no tendency to diminish with increase in the isize of the spherical particles. Study of the data in the table shows further that the ratio ϵ is not constant for each model, but varies in a definite and complicated way for each size of sphere so that no single conversion factor can be regarded as reliable.

Of all the models, the first (A) showed the greatest departures from the exact values. The values of volumes of capillary condensate derived from Model A were in all cases too high, exceeding the exact values 3-4 or more times, on the average. Model B also gives considerable departures from the exact values. The ratio ϵ according to this model shows departures from unity in both directions to the extent of 30-300%. Hence, in comparisons with experimental data, when the accuracy of the experiment is sufficiently high, neither model is satisfactory for the description of capillary-condensation phenomena in a system of extremely small spheres in contact. As regards the other models, the greatest discrepancy in Model C is about 40% and all the results are low; with Model D the greatest departure from exact calculation is about 25%, and the discrepancy is generally about 10-15% on one side

or the other of unity. Finally, Model E shows a maximum discrepancey of 30% and an average discrepancy of about 10% on one side or the other. Hence, in calculations of moderate accuracy, when the experimental error averages at about 10%, we may use Models D or E as schemes of approximation, but errors in individual values of volumes found in this way may be 25-30%. Calculations that we have not given here show that for cells formed by spheres of various radii in contact the departures from the exact values are still greater, from which it follows that in the problem under consideration calculations based on the assumption of a meniscus of circular profile are of only limited significance. It is possible that it will be more expedient to select an empirical equation for the relationship we have found between the volume of liquid and the dimensionless ratio of the Kelvin radius to the radius of a sphere.

SUMMARY

1. By comparison with exact calculations it was shown that approximate calculations of volumes of liquid held near the point of contact of two spheres during capillary condensation are not sufficiently reliable if it is assumed that the meniscus has a circular profile.

2. For an assembly of spheres of constant radius errors in individual values of the volumes may be 25-30% for the best schemes of approximation, in which a mean radius of curvature of the meniscus or mean curvature of the surface is introduced. With certain other possible simplifications, the error is still greater.

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Received January 20, 1957

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*Original Russian pagination. See C. B. Translation.
**In Russian.

SYNTHESIS OF THIOLS, DISULFIDES, AND SULFONIC ACIDS CONTAINING TRICHLOROMETHYL, DICHLOROVINYL, AND CARBOXY GROUPS

R. G. Petrova and R. Kh. Freidlina

Nesmeianov, Zakharkin, and Petrova [1] described the preparation of sulfides of the types $S[(CH_2)_nCH_2CCl_3]_2$, $S[(CH_2)_nCH=CCl_2]_2$ and $S[(CH_2)_nCH_2COOH]_2$ from $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes. We considered that it would be of interest to prepare compounds with other sulfur-containing functional groups from $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes, namely thiols, disulfides, and sulfonic acids of the types:

$HS(CH_2)_nCH_2CCl_3$; $HS(CH_2)_nCH=CCl_2$; $HS(CH_2)_nCOOR$; $[-S(CH_2)_nCH_2CCl_3]_2$;
(I) (II) (III) (IV)

$[-S(CH_2)_nCH=CCl_2]_2$; $[-S(CH_2)_nCOOR]_2$; $HO_3S(CH_2)_nCH_2CCl_3$;
(V) (VI) (VII)

$HO_3S(CH_2)_nCOOR$,
(VIII)

(R = H or alkyl)

These compounds and their derivatives are of interest as intermediaries in synthesis and also are possibly of interest as plasticizers [2], lubricating oils [3], emulsifiers, and detergents, and also for use in the preparation of synthetic resins [2].

There are no references in the literature to the synthesis of compounds of types (II), (IV), (V), and (VII). As regards compounds of type (I), there is mention in a patent of the preparation of 9,9,9-trichloro-1-nonanethiol from 1,1,1,9-tetrachlorononane. However, no information is given on the conditions of synthesis and the constants of the product [4]. As regards ω-mercapto-carboxylic acids (III), the lower members (C_2 and C_3) of this series have been prepared and studied in fair detail. Among sulfo-carboxylic acids of type (VIII), the acid $HO_3S(CH_2)_4COOH$, which is a sulfur analog of adipic acid, has not been described.

We prepared the dithio compounds of types (IV)-(VI) by the action of sodium disulfide on $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes, α,α,ω-trichloroalkenes, and ω-chloro-carboxylic acids. The chloro-disulfides obtained, and also 5,5'-dithiodivaleric esters, are high-boiling liquids which distill under reduced pressure without decomposition. The structure of bis-5,5,5-trichloropentyl disulfide was confirmed by its conversion into 5,5,5-trichloro-1-pentanesulfenyl chloride under the action of chlorine and into 5,5'-dithiodivaleric acid by hydrolysis. It should be noted that in the hydrolysis of bis-5,5,5-trichloropentyl sulfide in concentrated sulfuric acid, 5,5'-dithiodivaleric acid was isolated only in low yield due to resinification. This acid was obtained in good yield by reaction between sodium 5-chlorovalerate and sodium disulfide in aqueous solution. Oxidation of 5,5'-dithiodivaleric acid with 28% hydrogen perioxide in acetic acid gives a disulfoxide of composition $C_{10}H_{18}O_6S$.

The structure of 5,5'-dithiodivaleric acid was confirmed also by its reduction with zinc and sulfuric acid with formation of 5-mercaptovaleric acid. 5-Mercaptovaleric acid has been prepared previously [5] by the addition of thiolacetic acid to 4-pentenoic acid and subsequent hydrolysis:

$$CH_2=CHCH_2CH_2CO_2H + CH_3COSH \longrightarrow$$

$$\longrightarrow CH_3COSCH_2CH_2CH_2CH_2CO_2H \longrightarrow HSCH_2CH_2CH_2CH_2CO_2H$$

In this investigation no direct proof was given that the addition of thiolacetic acid to 4-pentenoic acid proceeded contrary to Markownikoff's rule and without isomerization of the original acid. When this mercaptovaleric acid was oxidized with iodine, dithiodivaleric acid was isolated. These methods for the preparation of mercapto-

valeric and dithiodivaleric acids are of no practical importance in view of their multistage character and the comparative difficulty of preparing the starting substances.

We prepared other mercapto compounds of types (I)-(III) by double decomposition of the corresponding ω-chloro compounds with sodium hydrosulfide. As by-products we always obtained the corresponding thio compounds. The sodium salts of the sulfonic acids (VII) and (VIII) were prepared by prolonged heating of the chloro compounds with sodium sulfite in an aqueous-alcoholic medium. Reaction between 1,1,5-trichloro-1-pentene and sodium sulfite was more complicated and gave not only sodium 5,5-dichloro-4-pentene-1-sulfonate, but also a com compound having two sulfo groups in its molecule. The sulfonates contain firmly bound water of crystallization, from which they can be freed only by prolonged heating at 120°.

TABLE

Formula of sulfonic acid	M.p. of thiouronium salt (°C)	Found (%)			Calculated (%)		
		C	H	N	C	H	N
$CCl_3(CH_2)_4SO_3H$	142			6,49 6,55			6,64
$CCl_3(CH_2)_6SO_3H$	140			6,37 6,27			6,45
$CCl_3(CH_2)_8SO_3H$	123	42,51 42,72	5,57 5,68	6,10 6,13	42,72	5,66	5,86
$C_2H_5OOC(CH_2)_4SO_3H$	105	47,61 47,86	6,10 6,31		47,87	6,38	

By the action of S-benzylthiouronium chloride in an aqueous-alcoholic medium the sodium sulfonates were converted into their thiouronium salts (see table).

EXPERIMENTAL

Bis-5,5,5-trichloropentyl Disulfide $[CCl_3-(CH_2)_4]S_2$. 1,1,1,5-Tetrachloropentane (42 g) was added to a solution of sodium disulfide prepared from 24 g of sodium sulfide ($Na_2S \cdot 9H_2O$) and 3.2 g of sulfur in 120 ml of ethanol, and the mixture was boiled with stirring for two hours. Alcohol was distilled off, the residue was poured into water, and the layers were separated. The oily layer was washed with water and dried with calcium chloride. The yield of crude bis-5,5,5-trichloropentyl disulfide was 37.3 g (90%); b.p. 215-218° (2 mm); $n^{20}D$ 1.5449; d^{20}_4 1,3895; found MR 93 96; calculated MR 93.72.

Found %: C 29.51; 29.39; H 3.99; 3.97; Cl 57.85; 58.03. $C_{10}H_{16}Cl_6S_2$. Calculated %: C 29.07; H 3.87; Cl 58.67.

5,5,5-Trichloro-1-pentanesulfenyl Chloride $ClS(CH_2)_4CCl_3$. A solution of 5 g of chlorine in carbon tetrachloride was added at a temperature of from −10° to −20° to a well stirred and cooled solution of 20.6 g of bis-5,5,5-trichloropentyl disulfide in dry carbon tetrachloride. The reaction mixture was stirred for one hour at below 0°, and solvent was then driven off at the water pump. The 5,5,5-trichloro-1-pentanesulfenyl chloride formed was distilled from the residue under reduced pressure. It was a liquid which, on standing in the air, liberated hydrogen sulfide; b.p. 96-98° (2 mm); $n^{20}D$ 1.5308; d^{20}_4 1.4250; found MR 52.46, calculated MR 52.76.

Found %: C 24.59; 14.85; H 3.16; 3.20; Cl 58.74; 58.63. $C_5H_8SCl_4$. Calculated %: C 24.79; H 3.31; Cl 58.67.

Bis-5,5-dichloro-4-pentenyl Disulfide $[CCl_2=CH(CH_2)_3]S_2$. From 17.5 g of 1,1,5-trichloro-1-pentene, 12 g of sodium sulfide ($Na_2S \cdot 9H_2O$), and 1.6 g of sulfur in 60 ml of ethanol we obtained 14.5 g of crude product. In its vacuum distillation we collected two fractions:

Fraction I, b.p. 174-178° (1.5-2 mm); 8.4 g.
Fraction II, b.p. 180-200° (2-3 mm); 4.3 g.

Fraction I was bis-5,5-dichloro-4-pentenyl disulfide; $n^{20}D$ 1.5592; d^{20}_4 1.3244; found MR 82.91; calculated MR 83.05.

Found %: C 35.42; 35.53; H 4.22; 4.02. $C_{10}H_{14}S_2Cl_4$. Calculated %: C 35.29; H 4.12.

The higher-boiling fraction probably contained trisulfide.

5,5'-Dithiodivaleric Acid $S_2[(CH_2)_4CO_2H]_2$. Sulfur (6.4 g) was added to a solution of 48 g of sodium sulfide in 50 ml of water, and the mixture was heated in a water bath until the sulfur dissolved completely. Addition was then made of sodium 5-chlorovalerate, prepared from 55 g of 5-chlorovaleric acid and 16 g of sodium hydroxide in 160 ml of water, and the solution was heated for two hours in a water bath. The mixture was cooled and acidified with dilute sulfuric acid; the precipitate formed was filtered off and washed with water until the acid reaction to Congo red disappeared. The yield of dry dithiodivaleric acid was 43.3 g (81%). After recrystallization from water, aqueous alcohol, and dichloroethane, it had m.p. 84.5-85° (the literature [5] gives 88-90°).

Found %: C 44.85; 54.01; H 6.70; 6.73; S 23.67; 23.77. $C_{10}H_{18}O_4S_2$. Calculated %: C 45.11; H 6.76; S 24.06.

Dithiodivaleric acid was prepared also by the hydrolysis of bis-5,5,5-trichloropentyl disulfide with concentrated sulfuric acid. In this reaction considerable resinification occurred, and the acid could be isolated only in low yield; m.p. 84-95° (from water). Oxidation of 5,5'-dithiodivaleric acid with excess of hydrogen peroxide in glacial acetic acid gave the corresponding disulfoxide $C_{10}H_{18}O_6S_2$, m.p. 118° (from alcohol).

Found %: C 40.14; 40.05; H 6.08; 6.15; S 21.77; 21.76. $C_{10}H_{18}O_6S_2$. Calculated %: C 40.26; H 6.04; S 21.44.

Diethyl 5,5'-dithiodivalerate had b.p. 178-183° (3.5 mm); $n^{20}D$ 1.4922; d^{20}_4 1.0865; found MR 85.92; calculated MR 86.01.

Found %: S 20.24; 19.85. $C_{14}H_{26}O_4S_2$. Calculated %: S 19.87.

Dibutyl 5,5'-dithiodivalerate had b.p. 210-213° (3 mm); $n^{20}D$ 1.4828; d^{20}_4 1.0294; found MR 104.83; calculated MR 104.54.

Found %: S 17.22; 17.08. $C_{18}H_{34}O_4S_2$. Calculated %: S 16.93.

Bis-2-ethylhexyl 5,5'-dithiodivalerate had b.p. 218-223° (2 mm); $n^{20}D$ 1.4778; d^{20}_4 0.9799; found MR 141.49; calculated MR 141.48.

Found %: S 13.76; 13.76. $C_{20}H_{50}O_4S_2$. Calculated %: S 13.06.

5-Mercaptovaleric Acid $HS(CH_2)_4CO_2H$. Zinc (24 g) and dilute sulfuric acid were added to 16.2 g of 5,5'-dithiodivaleric acid in 400 ml of water. The mixture was stirred at room temperature for 20 hours with periodic addition of sulfuric acid; it was then extracted with ether. The ether layer was washed with water, dried with sodium sulfate, and vacuum-distilled. The yield of 5-mercaptovaleric acid was 12.5 g (77%); b.p. 111-112° (5 mm); $n^{20}D$ 1.4880; d^{20}_4 1.1173; found MR 34.55; calculated MR 34.54. The literature [5] gives b.p. 110-112° (0.8 mm); $n^{20}D$ 1.4882; d^{20}_4 1.1195.

Found %: C 44.83; 44.73; H 7.52; 7.60; S 23.90; 23.84. $C_5H_{10}O_2S$. Calculated %: C 44.78; H 7.46; S 23.88.

5-Mercaptovaleric acid (7.5 g) was added dropwise to 100 ml of 30% HNO_3 heated in a water bath. The solution was then boiled for 30 minutes and set aside at room temperature. The precipitate that formed was filtered off, washed with water, and recrystallized from water; m.p. 117-118°. In admixture with the oxidation product of 5,5'-dithiodivaleric acid there was no depression of melting point.

Found %: C 40.39; 40.32; H 6.08; 6.02. $C_{10}H_{18}O_6S_2$. Calculated %: C 40.26; H 6.04.

The acid filtrate was not investigated.

Ethyl 5-Mercaptovalerate $HS(CH_2)_4CO_2C_2H_5$. A solution of 9.2 g of sodium in 300 ml of absolute alcohol was saturated with dry hydrogen sulfide. Ethyl 5-chlorovalerate (66 g) was added, and the mixture was boiled with stirring for two hours. Alcohol was distilled off, water was added to the residue, and the layers were separated. The oily layer was washed with water, dried with sodium sulfate, and vacuum-distilled.

Fraction I, b.p. 73-74° (3 mm); 26.6 g
Fraction II, b.p. 164-167° (1.5 mm); 10.5 g.

The lower-boiling fraction was ethyl 5-mercaptovalerate; $n^{20}D$ 1.4618; d^{20}_4 1.0018; found MR 43.72; calculated MR 43.99; yield 41%.

Found %: C 51.76; 51.77; H 8.75; 8.69; S 19.71; 19.68. $C_7H_{14}O_2S$. Calculated %: C 51.85; H 8.64; S 19.75.

The higher-boiling fraction was diethyl 5,5'-thiodivalerate; b.p. 164-167° (1.5 mm); $n^{20}D$ 1.4705; d^{20}_4 1.0380; found MR 78.02; calculated MR 78.16. The same ester, prepared by the esterification of 5,5'-thiodivaleric acid [6], had b.p. 169-170° (1.5 mm); $n^{20}D$ 1.4665; d^{20}_4 1.0315.

5,5,5-Trichloro-1-pentanethiol $HS(CH_2)_4CCl_3$. 1,1,1,5-Tetrachloropentane (42 g) was added to sodium hydrosulfide prepared from 5 g of sodium in 200 ml of absolute alcohol and hydrogen sulfide, and the solution was heated for two hours at 60-70°. The product, amounting to 21 g (51%), was 5,5,5-trichloro-1-pentanethiol; b.p. 77-78° (4 mm); $n^{20}D$ 1.5122; d^{20}_4 1.3050; found MR 47.73; calculated MR 47.68.

Found %: C 29.07; 29.12; H 4.12; 4.28; Cl 51.53, 51.25. $C_5H_9Cl_3S$. Calculated %: C 28.92; H 4.33; Cl 51.32.

We obtained also 5 g of bis-5,5,5-trichloropentyl sulfide, b.p. 182-183° (3 mm); when seeded, the product solidified completely (cf. [1]).

5,5-Dichloro-4-pentene-1-thiol $HS(CH_2)_3CH=CCl_2$. By reaction as described above between 30 g of 1,1,5-trichloro-1-pentene and sodium hydrosulfide in alcoholic solution we obtained 9 g (30%) of 5,5-dichloro-4-pentene-1-thiol; b.p. 63-64° (4 mm); $n^{20}D$ 1.5238; d^{20}_4 1.2460; found MR 41.98; calculated MR 42.36.

Found %: C 35.37; 35.53; H 4.74; 4.82; Cl 41.32; 41.81, $C_5H_8Cl_2S$. Calculated %: C 35.08; H 4.68; Cl 41.52.

7,7,7-Trichloro-1-heptanethiol $HS(CH_2)_6CCl_3$. Reaction between 47 g of 1,1,1,7-tetrachloroheptane and sodium hydrosulfide in alcohol solution gave 28 g (60%) of 7,7,7-trichloro-1-heptanethiol and 11.6 g of a higher-boiling substance consisting mainly of bis-7,7,7-trichloroheptyl sulfide. 7,7,7-Trichloro-1-heptanethiol has b.p. 98° (2 mm); $n^{20}D$ 1.5052; d^{20}_4 1.2240; found MR 56.94; calculated MR 57.08.

Found %: C 35.66; 35.90; H 5.47; 5.59. $C_7H_{12}Cl_3S$. Calculated %: C 35.67; H 5.52.

9,9,9-Trichloro-1-nonanethiol $HS(CH_2)_8CCl_3$. Reaction between 52 g of 1,1,1,9-tetrachlorononane and sodium hydrosulfide prepared from 5 g of sodium in 200 ml of absolute alcohol and hydrogen sulfide gave 21 g (41%) of 9,9,9-trichloro-1-nonanethiol; b.p. 139-142° (3.5 mm); $n^{20}D$ 1.4990; d^{20}_4 1.1632; found MR 66.51; calculated MR 66.17.

Found %: C 41.62; 41.61; H 6.62; 6.64; Cl 39.63; 39.90. $C_9H_{17}Cl_3S$. Calculated %: C 40.99; H 6.45; Cl 40.42.

There was a high-boiling fraction (17.5 g), probably the corresponding sulfide; it could not be vacuum-distilled without decomposition.

Sodium Salt of Ethyl 5-Sulfovalerate $NaO_3S(CH_2)_4CO_2C_2H_5$. A solution of 33 g of the ethyl 5-chlorovalerate in 100 ml of alcohol was added to a solution of 60 g of sodium sulfite ($Na_2SO_3 \cdot 7H_2O$) and 4 g of sodium iodide in 7 ml of water, and the mixture was boiled with stirring for 30 hours. Solvent was distilled off, and the dry residue was washed with alcohol and ether. It was then extracted with a large volume of acetone (about 3 liters). When the acetone solution was cooled, glistening white plates (25.4 g) of the sodium salt of ethyl 5-sulfovalerate were precipitated (51.6% yield on the amount of ethyl 5-chlorovalerate taken). The crystals were dried over phosphoric oxide.

Found %: C 34.87; 34.84; H 5.75; 5.66; S 13.30; 13.18. $C_7H_{13}O_5SNa \cdot 0.5H_2O$. Calculated %: C 34.85; H 5.80; S 13.27.

After being dried at 120° for 12 hours, the substance was again analyzed.

Found %: C 35.72; 35.85; H 5.62; 5.61. $C_7H_{13}O_5SNa$. Calculated %: C 36.20; H 5.60.

Sodium 5,5,5-Trichloro-1-pentanesulfonate $NaO_3S(CH_2)_4CCl_3$. A mixture of a solution of 42 g of 1,1,1,5-tetrachloropentane in 80 ml of alcohol and a solution of 50 g of sodium sulfite ($Na_2SO_3 \cdot 7H_2O$) and 5 g of sodium

iodide in water was boiled for 24 hours. The supension of "fluffy" Precipitate I was separated from the lower crystalline Precipitate II. Both precipitates were filtered off and washed with acetone. Precipitate I (14 g) was sparingly soluble in cold water and in alcohol and was insoluble in acetone; it consisted of sodium 5,5,5-trichloro--1-pentanesulfonate. The aqueous-alcoholic filtrate was vacuum-evaporated to dryness; the residue was mixed with Precipitate II (20.5 g) and treated with water to remove sodium sulfate. The undissolved sodium 5,5,5-trichloro--1-pentanesulfonate was filtered off and washed with acetone (15.4 g). The total yield of crude salt was 53% on the amount of 1,1,1,5-tetrachloropentane taken. This salt was recrystallized from alcohol and dried over phosphoric oxide.

Found %: C 19.87; 20.02; H 3.14; 3.16; Cl 35.98; 36.18. $C_5H_8Cl_3O_3SNa \cdot H_2O$. Calculated %: C 20.30; H 3.38; Cl 36.04.

Sodium 7,7,7-Trichloro-1-heptanesulfonate $NaSO_3(CH_2)_6CCl_3$. A reaction mixute consisting of a solution of 47 g of 1,1,1,7-tetrachloroheptane in 80 ml of alcohol and a solution of 25 g of sodium sulfite and 5 g of sodium iodide in water was boiled with stirring for 40 hours. The aqueous-alcoholic solution was decanted from Precipitate II, and it yielded Precipitate I, which consisted of sodium 7,7,7-trichloro-1-heptanesulfonate. Both precipitates were washed with acetone and ether. The weight of I was 10.8 g. Precipitate II (19.5 g) was recrystallized from water. This gave a further 5.2 g of sodium 7,7,7-trichloro-1-heptanesulfonate. The ether-acetone filtrate yielded 18 g of unchanged 1,1,1,7-tetrachloroheptane. The yield was 42.5% on the 1,1,1,7-tetrachloroheptane that reacted. The salt obtained was recrystallized from water and dried over phosphoric oxide.

Found %: C 26.47; 26.60; H 4.12; 4.33; Cl 33.64; 33.52. $C_7H_{12}Cl_3SNa \cdot 0.5H_2O$. Calculated %: C 26.70; H 4.10; Cl 33.86.

Sodium 9,9,9-Trichloro-1-nonanesulfonate $NaO_3S(CH_2)_8CCl_3$. Reaction between 53 g of 1,1,1,9-tetrachlorononane in 150 ml of alcohol, 50 g of sodium sulfite ($NaSO_3 \cdot 7H_2O$), and 6 g of sodium iodide at the boil for 40 hours with subsequent treatment as in the preceding experiment gave 12.9 g (56% on the amount of 1,1,1,9-tetrachlorononane that reacted) of sodium 9,9,9-trichloro-1-nonanesulfonate. The product was recrystallized from water and dried over phosphoric oxide.

Found %: C 31.59; 31.64; H 5.06; 4.88; Cl 30.32; 30.35. $C_9H_{16}Cl_3O_3SNa \cdot 0.5H_2O$. Calculated %: C 31.53; H 4.96; Cl 31.09.

1,1,1,9-Tetrachlorononane recovered unchanged amounted to 35 g.

SUMMARY

Starting from α,α,α,ω-tetrachloroalkanes, trichloroalkenes of structure $CCl_2 = CH(CH_2)_nCl$, and ω-chloro carboxylic acids, we obtained ithio, mercapto, and sulfo compounds and some of their derivatives of structure: $[CCl_3(CH_2)_4]_2S_2$; $[CCl_2 = CH(CH_2)_3]_2S_2$; $[ROOC(CH_2)_4]_2S_2$ (in which R = H, C_2H_5; n-C_4H_9; $C_4H_9-\underset{\displaystyle C_2H_5}{\underset{|}{CH}}-CH_2$);

$CCl_3(CH_2)_4SCl$; $CCl_3(CH_2)_nSH$ (in which n = 4,6,8); $CCl_2=CH(CH_2)_3SH$; $ROOC(CH_2)_4SH$ (in which R = H, C_2H_5); $CCl_3(CH_2)_nSO_3Na$ (in which n = 4,6,8); $C_2H_5OOC(CH_2)_4SO_3Na$.

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Received November 17, 1956

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REACTIONS OF FLUOROOLEFINS

COMMUNICATION 7. ADDITION OF ACID CHLORIDES TO VINYLIDENE FLUORIDE AND TRIFLUOROETHYLENE

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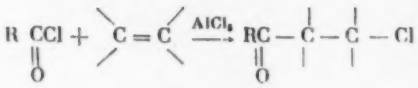
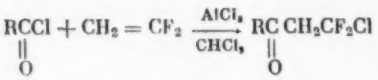
The addition of carboxylic acid chlorides to olefins, a reaction discovered by Kondakov [1, 2] and developed later by other investigators [3-7], is now a preparative method of obtaining β-haloketones:



The reaction is generally carried out by the addition of the olefin to a stirred cooled solution of the complex of the acid chloride with $AlCl_3$ in such solvents as CH_2Cl_2, $ClCH_2CH_2Cl$, $CHCl_3$, $C_6H_5NO_2$, or in excess of the acid chloride.

Chloroolefins can also react in this way. Thus, by reaction of chloroacetyl chloride with 1,2-dichloroethylene and in trichloroacetyl chloride with trichloroethylene [3] the corresponding saturated polychloro-ketones are formed. On the other hand, the ketones formed by the addition of acetyl chloride to vinyl chloride [3] and to vinylidene chloride [8] are so unstable that only the corresponding unsaturated ketones can be isolated. We have shown that fluoroolefins such as vinylidene fluoride and trifluoroethylene can combine with carboxylic acid chlorides in presence of anhydrous $AlCl_3$ with formation of the corresponding fluoro-ketones.

Acetyl, propionyl, and butyryl chlorides very readily add to vinylidene fluoride at a temperatureof from −5° to −10° in presence of equivalent amounts of $AlCl_3$ in dry chloroform with formation of alkyl 2-chloro-2,2-difluoroethyl ketones in yields of 44, 48, and 33 per cent, respectively.



$R = CH_3$; C_2H_5; P-C_3H_7.

At the same time substances in which fluorine is partially or completely replaced by chlorine and products of further condensation are formed. Alkyl 2-chloro-2,2-difluoroethyl ketones are colorless mobile liquids which have a sharp odor and a lacrimatory effect; they can be preserved in a refrigerator for a fairly long time, but spontaneous liberation of hydrogen chloride occurs.

The reaction between trifluoroethylene and acetyl chloride was carried out by shaking a mixture of the olefin, an equimolecular amount of $AlCl_3$, and excess of acetyl chloride for a short time in an autoclave at room temperature; 4-chloro-4,4-difluoro-2-butanone was obtained in 34% yield:

This ketone is a pleasantly-smelling colorless liquid; it is more stable, and it does not give up hydrogen chloride spontaneously.

We based our views on the direction of addition of acid chlorides to fluoroolefins on the polarity of the reactants. A carbon atom carrying two fluorine atoms is charged positively with respect to a carbon carrying no fluorine or only one fluorine atom, this being a consequence of the strong polarization of the C–F bond. This direction of addition is confirmed by the tendency of the ketones obtained to lose hydrogen chloride. Thus, treatment of 4-chloro-4,4-difluoro-2-butanone with triethylamine in dimethyl ether at room temperature, or even at –80°, resulted in the quantitative formation of triethylamine hydrochloride and the isolation of a substance which could not be fully purified owing to its instability. However, analysis indicates that it was probably the hydrated form of the previously unknown 3,4,4-trifluoro-3-buten-2-one. The composition of the 2,4-dinitrophenylhydrazone of this substance also corresponded to the hydrate, which is not surprising, because the tendency of fluoro ketones to form stable hydrates is well known.

EXPERIMENTAL

Reaction of Vinylidene Fluoride with Acid Chlorides. A mixture of 26.7 g (0.2 mole) of anhydrous aluminum chloride and 75 g of dry chloroform was prepared in a flask fitted with stirrer, tube for admittance and exit of gases, and thermometer, and 0.2 mole of the acid anhydride was added. When the aluminum chloride had dissolved, the mixture was cooled to room temperature and was stirred vigorously while dry vinylidene fluoride was passed in. When the temperature began to rise, the flask was cooled and the further passage of gas was carried out at a temperature of from –10° to –5° until absorption ceased. The reaction mixture was then decomposed by stirring it with ice and hydrochloric acid (50 ml); the organic layer was separated, and the aqueous layer was extracted with ether. The extract was combined with the organic layer, and the whole was dried with magnesium sulfate. Solvent was distilled off under reduced pressure, and the residue was vacuum-distilled. In this way we prepared the following fluoro ketones.

4-Chloro-4,4-difluoro-2-butanone. This was prepared by addition of CH_3COCl to $CH_2=CF_2$; yield 44.5%; b.p. 40-41° (25 mm); $n^{20}D$ 1.3860; d^{20}_4 1.2842, found MR 25.97; calculated for $C_4H_5OF_2Cl$ MR 25.83.

Found %: C 33.58; 33.61; H 3.54; 3.50; F 26.77; 26.54; Cl 25.20; 25.22. $C_4H_5OF_2Cl$. Calculated %: C 33.69; H 3.53; F 26.55; Cl 24.90.

2,4-Dinitrophenylhydrazone, m.p. 114-115.5° (from alcohol).

Found %: N 16.88; 16.89. $C_{10}H_9O_4N_4F_2Cl$. Calculated %: N 17.35.

1-Chloro-1,1-difluoro-3-pentanone. This was prepared by addition of C_2H_5COCl to $CH_2=CF_2$; yield 48%; b.p. 56-57° (30 mm); $n^{20}D$ 1.3974; d^{20}_4 1.2357; found MR 30.58; calculated for $C_5H_7OF_2Cl$ MR 30.45.

Found %: C 37.89; 38.00; H 4.56; 4.48. $C_5H_7OF_2Cl$. Calculated %: C 38.35; H 4.50.

2,4-Dinitrophenylhydrazone, m.p. 95-98° (from alcohol).

Found %: N 16.85; 16.75. $C_{11}H_{11}O_4N_4F_2Cl$. Calculated %: N 16.63.

1-Chloro-1,1-difluoro-3-hexanone. This was prepared by addition of $n\text{-}C_3H_7COCl$ to $CH_2=CF_2$, yield 33%; b.p. 64-65° (22 mm); $n^{20}D$ 1.4030; d^{20}_4 1.1927; found MR 35.00; calculated for $C_6H_9O_2FCl$ MR 35.07.

Found %: C 42.16; 42.21; H 5.24; 5.19. $C_6H_9OF_2Cl$. Calculated %: C 42.24; H 5.32.

Reaction of Trifluoroethylene with Acetyl Chloride. In each of two 70-ml metal test tubes 13.3 g (0.1 mole) of anhydrous aluminum chloride was placed; the test tubes were cooled to –30°, and 31 ml of acetyl chloride was added to each. The test tubes were then cooled to –80°, 12 g of liquid trifluoroethylene was added to each, and they were hermetically sealed and shaken for one hour at room temperature. Unchanged trifluoroethylene (3.8 liters) was removed from the reaction mixture, acetyl chloride was distilled off (in a vacuum at room temperature), and the residue was poured into ice water. The red oil that separated was dried over magnesium sulfate, and all that would come over below 103° was distilled off, the oil bath being heated to 140°. The distillate was washed with sodium bicarbonate solution until it had an alkaline reaction; it was then washed with water and dried over magnesium sulfate. Distillation gave 13 g (34% on the olefin that reacted) of 4-chloro-3,4,4-trifluoro-2-butanone; b.p. 99-100°; $n^{20}D$ 1.3638; d^{20}_4 1.3752; found MR 26.00; calculated for $C_4H_4OF_3Cl$ MR 25.97.

Found %: C 30.17; 30.09; H 2.72; 2.78; F 34.50; Cl 22.59. $C_4H_4OF_3Cl$. Calculated %: C 29.91; H 2.49; F 35.50; Cl 22.16.

2,4-Dinitrophenylhydrazone, m.p. 101° (from benzene-methanol).

Found %: N 16.40; 16.29. $C_{10}H_8O_4N_4F_3Cl$. Calculated %: N 16.40.

By vacuum distillation of the residue remaining after the collection of 4-chloro-3,4,4-trifluoro-2-butanone we isolated 15 g of a substance of b.p. 92° (5 mm) and $n^{20}D$ 1.4600. On standing it solidified; m.p. 32°. The substance had an acid reaction. The analysis and molecular weight corresponded to $C_7H_{10}O_4FCl_3$. The substance was not investigated further.

Dehydrochlorination of 4-Chloro-3,4,4-trifluoro-2-butanone. In each of two 100-ml glass ampoules 7.5 g of 4-chloro-3,4,4-trifluoro-2-butanone was placed and cooled to −40°. In each tube 60 ml of dimethyl ether was condensed, and 6.5 ml of previously cooled triethylamine was added gradually. The ampoules were sealed and left for three hours at room temperature. The precipitate of amine hydrochloride was filtered off and washed with dimethyl ether. Solvent was distilled from the combined filtrate through a Podbielniak column, and the residue was distilled in a vacuum at room temperature into a received cooled to −70°. The distillate was redistilled at atmospheric pressure. The product, amounting to 2.25 g (21%), was considered to be the hydrate of 3,4,4-trifluoro-3-buten-2-one and was obtained as a colorless extremely volatile liquid of characteristic odor. The substance underwent some resinification during distillation; b.p. 70-72°; $n^{20}D$ 1.3180; d^{20}_4 1.2972.

Found %: C 33.94; 33.89; H 4.40; 4.10. $C_4H_3OF_3 \cdot H_2O$. Calculated %: C 33.80; H 3.52.

2,4-Dinitrophenylhydrazone, m.p. 110-110.5° (from methanol-benzene).

Found %: N 17.40; 17.54. $C_{10}H_7O_4N_4F_3 \cdot H_2O$. Calculated %: N 17.38.

SUMMARY

1. It was shown that it is possible in principle to added acid chlorides to fluoroolefins, which were here exemplified by vinylidene fluoride and trifluoroethylene.

2. 4-Chloro-4,4-difluoro-2-butanone, 1-chloro-1,1-difluoro-3-pentanone, 1-chloro-1,1-difluoro-3-hexanone, and 4-chloro-3,4,4-trifluoro-2-butanone were prepared.

Received November 3, 1956

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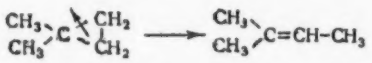
ISOMERIZATION OF 1,1,2-TRIMETHYLCYCLOPROPANE IN PRESENCE OF PALLADIZED AND PLATINIZED CHARCOALS

M. Iu. Lukina, S. V. Zotova, and B. A. Kazanskii

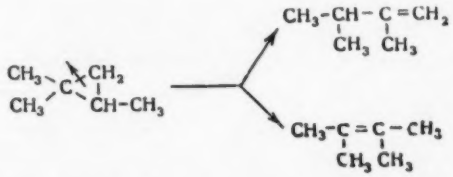
In presence of certain catalysts (alumina, silica gel, and platinum black) cyclopropane and its homologs can isomerize into olefins. Thus, Ipat'ev and Gun [1] showed that cyclopropane, passed at low space velocities over alumina at 370-385°, is converted into propene to the extent of 20%. When it is passed at the same space velocity through an empty tube heated to the same temperature, only 1-2% of propene is formed.

As the same authors showed [1], 1,1-dimethylcyclopropane has a much greater tendency to isomerize than cyclopropane itself: at 340° in presence of alumina it is converted completely into 2-methyl-2-butene:

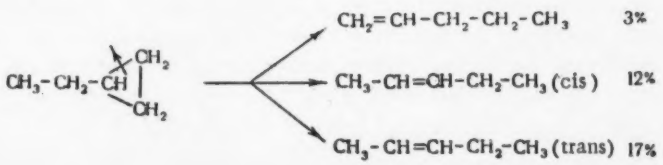


The isomerization of ethylcyclopropane at 300-310° in presence of asbestos-alumina was studied by Rozanov [2]. The author considers the reaction to be

Petrov [3] studied the isomerization of 1,1,2-trimethylcyclopropane and found that isomerization proceeds to completion at 200° in presence of alumina in accordance with the scheme:

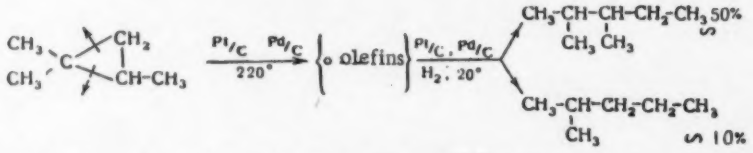


The isomerizing effect of silica gel on the three-membered cycle of Δ^3-carene was observed by Arbuzov and Isaeva [4]. In the catalytic treatment of 1,1,2-trimethylcyclopropane with silica gel, Boord and co-workers [5] observed a change in the refractive index of the hydrocarbon which they ascribed to isomerization into olefins. Kazanskii and co-workers [6] studied the isomerization for the case of ethylcyclopropane and found that, under the conditions of chromatographic analysis on silica gel, this hydrocarbon is isomerized into olefins to the extent of 32% in accordance with the scheme:



The isomerizing effect of platinum on a three-membered cycle was first noted by Tanatar [7]. He showed that cyclopropane, kept for five months over platinum black in sealed tubes, is converted into propene to the extent of 20-30%. Ipat'ev and Gun [1] found that in the passage of cyclopropane over platinum black at 200° at low space velocity only 4-5% of propene is formed. With rise in temperature to 315° the amount of propene rises to 29%. These results are not in accord with the behavior, as reported by Petrov [3], of 1,1,2-trimethylcyclopropane, which did not isomerize when passed over platinum at 300°.

In a study of the hydrogenolysis of alkylcyclopropanes in presence of platinum and palladium catalysts we considered it to be of interest to investigate the isomerizing effects of these catalysts on the cyclopropane system, particularly as the literature cited above contains contradictions. We chose 1,1,2-trimethylcyclopropane for investigation; as catalysts we used platinized and palladized charcoals in absence of hydrogen. Our investigation showed that above 200° both palladized and platinized charcoals brought about appreciable isomerization of 1,1,2-trimethylcyclopropane into olefins. The extent of isomerization increased with rise in temperature to 250°, but remained constant with further rise in temperature to 280°. Experiments in which catalyzate was collected in quantity were carried out at 220°. Analysis of the catalyzate showed that in presence of either catalyst isomerization proceeds to the extent of about 60% and it is mainly the bond between the most and least hydrogenated carbon atoms of the ring that is broken, which is in accord with data in the literature [2-4, 6] on the isomerization of alkylcyclopropanes in presence of other catalysts. However, the largeness of the amount of catalyzate obtained in the experiment with palladized charcoal and the use of a highly efficient fractionation column enabled us to detect reaction with rupture of the other bond attached to the quaternary carbon atom. The bond between the most hydrogenated carbon atoms (the bond which breaks in the hydrogenolysis of alkylcyclopropanes [8]) remains intact in the isomerization. The isomerization, therefore, proceeds as follows:



It was confirmed that there is no isomerization in absence of catalyst: when 1,1,2-trimethylcyclopropane was passed at 220° through a tube filled with quartz, it was unaffected.

EXPERIMENTAL

The 1,1,2-trimethylcyclopropane had the following properties: b.p. 52.5° (760 mm), $n^{20}D$ 1.3862; d^{20}_4 0.6947.

TABLE 1

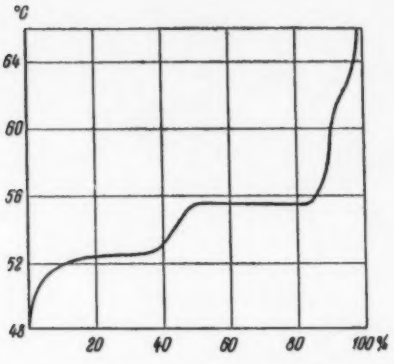
Hydrocarbon	B.p. (°C at 760 mm)	$n^{20}D$	d^{20}_4
1,1,2-trimethylcyclopropane [5]	52.55	1.3864	0.6947
2-Methylpentane [9]	60.271	1.37145	0.65315
2,2-Dimethylbutane [9]	49.741	1.36876	0.64916
2,3-Dimethylbutane [9]	57.988	1.37495	0.66164

Experimental Procedure. The experiments were carried out in a flow system in the way that we have described on several occasions [8]. The catalyst was reduced in a stream of hydrogen at 300°, after which the temperature was lowered to the required value, passage of hydrogen was stopped, and hydrogen adsorbed by the catalyst was removed from its surface by means of certain amount of 1,1,2-trimethylcyclopropane, which was then rejected. 11,1,2-Trimethylcycloprpopane was then passed over the catalyst at a space velocity of 0.2 in a feeble stream of nitrogen. The catalyzate corrected was hydrogenated in the cold and fractionated.* The constants of the hydrocarbons which could be present in the mixture obtained are given in Table 1.

* An attempt to fractionate the unsaturated catalyzates into pure substances was not successful.

1. Isomerization of 1,1,2-Trimethylcyclopropane in Presence of Palladized Charcoal

1,1,2-Trimethylcyclopropane was passed through the catalysis tube, which contained 50 ml of 20% palladized charcoal prepared by Zelinskii's method [10].* The catalyzate had $n^{20}D$ 1.3940 and bromine value 121, which corresponds to a 63% content of unsaturated hydrocarbons. After hydrogenation in a long-necked flask at room temperature in presence of palladized charcoal, 78.0 g of the mixture was fractionated through a column of 100 theoretical plates. The fractionation results are given in Table 2 and in the figure.



From a comparison between Table 1 and 2 we may conclude that Fraction VII was 2,3-dimethylbutane and Fraction IX (and Fraction X partially) was 2-methylpentane. Fractions II-IV were unchanged 1,1,2-trimethylcyclopropane. Fractions V, VI, and VIII were intermediate fractions. Fraction I contained 1,1,2-trimethylcyclopropane and probably very small amounts of 2,2-dimethylbutane, which could be formed by hydrogenolysis of 1,1,2-trimethylcyclopropane by hydrogen dissolved in the palladium. Hence, according to the fractionation results, isomerization proceeded to the extent of about 55%: about 45% of 2,3-dimethylbutane and about 10% of 2-methylpentane.

TABLE 2

Fraction	Amount (g)	B.p. (°C at 760 mm)	n_D^{20}	d_4^{20}
I	8,9	48,6—52,0	1,3800	0,6790
II	8,7	52,0—52,4	1,3857	0,6943
III	8,5	52,4—52,5	1,3862	0,6944
IV	3,2	52,5—52,9	1,3861	0,6946
V	7,7	52,9—57,3	1,3810	—
VI	3,2	57,3—57,6	1,3760	—
VII	25,4	57,6—57,7	1,3750	0,6612
VIII	4,6	57,7—59,8	1,3730	0,6565
IX	1,4	59,8—61,0	1,3717	0,6537*
X	5,3	61,0—86,4	1,3730	0,6548

Taken 78.0 g, distilled 76.9 g, losses 1.1 g.

*22 ml of n-octane was added.

2. Isomerization of 1,1,2-Trimethylcyclopropane in Presence of Platinized Charcoal

Determination of Temperature required for Reaction. 1,1,2-Trimethylcyclopropane was passed at various temperatures through the catalysis tube containing 10 ml (3.05 g) of 20% platinized charcoal prepared by Zelinskii's method [10].**. The results of the experiments are given in Table 3.

On the basis of the data in Table 3 we may conclude that at 200° isomerization, if it occurs at all, occurs only to a slight extent; at 250° the amount of unsaturated compounds in the catalyzate is much greater; and with further rise in temperature to 280° this amount remains unchanged.

*The catalyst had the following characteristics: when cyclohexane of $n^{20}D$ 1.4260 was passed through it at 300° at a space velocity of 0.2, the resulting catalyzate had $n^{20}D$ 1.4435.

**The characteristics of the catalyst are given in previous papers [8].

Isomerization. 1,1,2-Trimethylcyclopropane (39 ml, i.e., 27.3 g) was passed through the catalysis tube, which contained 20 ml of platinized charcoal. The catalyzate (34 ml) was reduced in alcoholic solution with hydrogen in a long-necked flask at room temperature in presence of 0.5 g of platinized charcoal. The mixture of hydrocarbons was steam-distilled, separated, dried, and fractionated through a column of 40 theoretical plates. The fraction results are given in Table 4.

TABLE 3

Experiment No.	Temperature (°C)	Space velocity (hour $^{-1}$)	$n^{20}D$	Reaction with bromine water
1	200	0.2	1.3868	Not decolorized
2	220	0.2	1.3922	Slowly decolorized
3	250	0.2	1.3972	Immediately decolorized
4	280	0.2	1.3970	Immediately decolorized

TABLE 4

Fraction	Amount (g)	B.p. (°C at 760 mm)	n_D^{20}	d_4^{20}
I	6,0	53,3—58,1	1,3790	0,6751
II	2,0	58,1—58,2	1,3749	0,6609
III	3,3	58,2—58,4	1,3748	0,6609
IV	2,7	58,4—58,7	1,3740	—

Taken 17.4 g (28 ml), distilled 14.0 g, residue 2.6 g, losses 0.6 g.

Comparison of the data in Table 4 with the constants of hydrocarbons given in Table 1 enables us to conclude that Fraction I was a mixture of 1,1,2-trimethylcyclopropane with 2,3-dimethylbutane and Fractions II and III were 2,3-dimethylbutane. Fraction IV was probably an intermediate fraction between 2,3-dimethylbutane and 2-methylpentane, which was present in the residue. The smallness of the amount of catalyzate and the relatively low efficiency of the column did not permit us to isolate the hydrocarbons in the pure state. The composition of the catalyzate was about the same as in the experiment with palladized charcoal, except that in this case Fraction I did not appear to contain any 2,2-dimethylbutane.

Experiments in Absence of Catalyst. Finely divided quartz glass was boiled with aqua regia, washed with water, and dried; 10 ml of it was placed in the catalysis tube. The tube was heated to 300°, the temperature was lowered to 220°, and 5 ml of 1,1,2-trimethylcyclopropane was passed through the quartz in a feeble stream of nitrogen at a space velocity of 0.2 hour^{-1}. The catalyzate had $n^{20}D$ 1.3862; and d^{20}_4 0.6948, i.e., did not differ from the original 1,1,2-trimethylcyclopropane; a test with bromine water was negative.

SUMMARY

1. It was found that 1,1,2-trimethylcyclopropane, passed at 220° over platinized or palladized charcoal at a space velocity of 0.2 hour^{-1}, is isomerized to the extent of about 60% into a mixture of olefins.

2. It was shown that, in absence of catalyst, the hydrocarbon remains unchanged under these conditions.

3. It was found that in isomerization the point of bond rupture in the ring is different from that found in hydrogenolysis; the bonds attached to the quaternary carbon atom are broken, mainly the bond between the most and least hydrogenated atoms of the ring.

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Received October 19, 1956

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* Original Russian pagination. See C. B. Translation.
** In Russian.

TRANSFORMATIONS OF n-HEPTANE OVER OXIDE – METAL CATALYSTS IN A FLOW SYSTEM IN PRESENCE OF HYDROGEN UNDER PRESSURE

Kh. M. Minachev, N. I. Shuikin, and L. M. Feofanova

In previous papers [1-7] we have reported experimental results obtained in the study of the high-temperature transformations of cyclohexanes, cyclopentanes, and n-alkanes in a flow system over oxide-metal catalysts in presence of hydrogen at high pressure. These investigations, which were directed mainly at the determination of the specificity of various metals of Group VIII in its relation to their chemical nature and the chemical nature of the carrier for the carrying out of the transformations of hydrocarbons of various classes, have enabled us to establish interesting regularities in the catalytic properties of these metals.

Without discussing the results obtained in detail we may point out that in some cases not only the chemical nature of the metal, but also the nature of the carrier, had a considerable effect on the extent and course of the transformations undergone by the hydrocarbon. Thus, in the study of the transformations of ethylcyclopentane over Pt, Pd, Rh, and Ru [1, 2] supported by Al_2O_3 and SiO_2, it was shown that the formation of toluene from this hydrocarbon is determined more by the chemical nature of the carrier than by that of the metal deposited on that carrier. Whereas in the treatment of ethylcyclopentane over $Pt-Al_2O_3$, $Pd-Al_2O_3$, $Rh-Al_2O_3$ and $Ru-Al_2O_3$ at 460° and 20 atm a large amount of toluene (40-45%) was formed, under the same conditions in presence of the same metals supported by silica dehydroisomerization (ring enlargement with subsequent dehydrogenation) occurred only to a small extent. The toluene contents of the catalyzates were only 5.8-8.1%, and in the presence of $Ru-SiO_2$ only hydrogenolysis of ethylcyclopentane to n-heptane was observed.

The present paper reports experimental results on the transformations of n-hetpane over Pt, Pd, and Rh supported by alumina. Results on the catalytic transformations of this hydrocarbon over Pt, Pd, and Rh supported by SiO_2 were reported in one of our previous papers [3]; in this it was shown that, under the given conditions, part of the heptane was aromatized to toluene and part was isomerized and hydrogenolyzed to C_5-C_7 isoalkanes. The contents of the latter were 45% over $Pt-SiO_2$, 20% over $Pd-SiO_2$, and 2.7% over $Rh-SiO_2$. With respect to the amounts of aromatic hydrocarbons formed (toluene with some benzene and xylenes) the catalysts fell in the following series: Pt > Pd > Rh.

EXPERIMENTAL

We described the preparation of the catalysts, their properties, the experimental procedure, the apparatus, and the method of investigating the catalyzates in previous papers [3, 4]. The experiments on the transformations of heptane over $Rh-Al_2O_3$ and $Pd-Al_2O_3$ were carried out at 450° at a hydrogen pressure of 20 atm and with a space velocity of feed of the original hydrocarbon of 1.0-1.1 $hour^{-1}$; the molar ratio of hydrogen to hydrocarbon was 5 : 1. In the case of $Pt-Al_2O_3$ all experiments were carried out at 400° with a space velocity of feed of hydrocarbon of 0.41-0.42 $hour^{-1}$; the remaining conditions were the same as those in the experiments with palladium and rhodium catalysts. The amount of catalyst taken in the reactor was 50 ml. Over each catalyst 200-230 g of heptane was passed. The aromatic hydrocarbons were adsorbed chromatographically, and the naphthene-paraffins were subjected to precision fractionation and Raman-spectrum analysis. Spectrum analysis was carried out only when the presence of naphthenes was postulated after the aniline points of the individual fractions had been determined. The table give the properties of the catalyzates.

The results given in the table indicate that the conversion of heptane over $Pt-Al_2O_3$ at 400° at a space velocity of 0.41 $hour^{-1}$ is greater than 60%. Comparison of the properties of the heptane catalyzate obtained over

$Rh-Al_2O_3$ with that obtained over $Pd-Al_2O_3$ shows that the rhodium catalyst was more active both in the dehydrocyclization and in the isomerization of heptane than $Pd-Al_2O_3$. We must point out that approximately the same results were obtained in the recent work of Hettinger and others [8] in the dehydrocyclization of heptane over $Pd-Al_2O_3$ and $Rh-Al_2O_3$ catalysts.

TABLE

Properties of Heptane Catalyzates Obtained in Presence of Pt-, Rh-, and Pd-Alumina Catalysts

Catalyst	Temp. of experiment (°C)	Properties of catalyzate			Conversion (% by weight on catalyzate)	Composition of gas	
		$n^{20}D$	d^{20}_4	Content of aromatic hydrocarbons (% by volume)		H_2	C_nH_{2n+2}
0.5 % $Pt-Al_2O_3$	400	1.3914	0.6818	2.0	62.8	97.2	2.8
1% $Rh-Al_2O_3$	450	1.3938	0.6880	6.0	25.1	92.0	8.0
1% $Pd-Al_2O_3$	450	1.3920	0.6860	4.5	16.3	94.6	5.4

Before the separation of aromatic hydrocarbons, all catalyzates were first freed from hydrocarbons boiling below 40°. Thus, from the catalyzate obtained over $Pt-Al_2O_3$ we isolated 1.8 g (0.9% on the catalyzate) of isoprentane and 4.2 g (2.1% on the catalyzate) of n-pentane, and from the catalyzate obtained over $Rh-Al_2O_3$ we isolated 6.6 g (about 2.2%) of isopentane and 4.9 g (about 2%) of n-pentane. From the catalyzate obtained in the treatment of heptane over $Pd-Al_2O_3$ we isolated a fraction boiling over the range 29-38° in an amount of only 1.4 g (0.7% on catalyzate). The aromatic fraction isolated by adsorption on silica gel corresponded in properties to almost pure toluene in the case of all three catalyzates.

The part of the catalyzate remaining after the removal of aromatic hydrocarbons was fractionated through a column of 33 theoretical plates, and the narrow fractions obtained were investigated by the Raman method. In the fractions isolated from the catalyzate obtained over $Pt-Al_2O_3$ we identified unchanged heptane, 2-methylpentane, hexane, 2,2,3-trimethylbutane, 2,2-dimethylpentane, 3,3-dimethylpentane, 2,4-dimethylpentane, 2-methylhexane, 3-methylhexane, and 3-ethylpentane. Also, in the Raman spectrum of the 65-75° fraction we observed lines indicating the presence of methylcyclopentane.

In the catalyzates obtained over $Rh-Al_2O_3$ and $Pd-Al_2O_3$ we identified almost all the hydrocarbons detected in the $Pt-Al_2O_3$ catalyzate with the exception of 2,2,3-trimethylpentane and 3-ethylpentane. However, in these catalyzates we detected appreciable amounts of cyclopentane hydrocarbons. Thus, in the 75-90° fraction of the $Pd-Al_2O_3$ catalyzate, apart from 2,4-dimethylpentane (about 15%) and 2-methylhexane (about 72%), we detected 1,2-dimethylcyclopentane (about 8%). The 97-102.5° fraction contained not only 88% of heptane, but also about 12% of ethylcyclopentane. The 75-90° fraction of the $Rh-Al_2O_3$ catalyzate contained not only 2,4-dimethylpentane, 3-methylhexane, and 2-methylhexane, but also about 5% of 1,2-dimethylcyclopentane.

When we compared the present results with those of our previous investigation [3] on the transformations of heptane over Pt, Pd, Ru, and Rh supported by silica, a substantial difference is observed. Thus, in the case of $Rh-Al_2O_3$ the content of saturated hydrocarbons in the gas was only one-eighth (see table) of that obtained under similar conditions in the case of $Rh-SiO_2$. Moreover, in our previous investigation we were unable to establish the presence of cyclopentanes in the heptane catalyzates, whereas in the catalyzates obtained in the present investigation they were present in appreciable amount. The presence of cyclopentanes in heptane catalyzates shows that they are formed not only under ordinary pressure at 310-215° over platinized charcoal, as shown by Kazanskii, Liberman, and co-workers [9, 10], but also under conditions differening greatly from these. Also, both from the present results and those reported previously [5-7] it follows that the synthesis of cyclopentanes from n-alkanes is observed not only over $Pt-Al_2O_3$ and platinized aluminum silicate, but also over Rh and Pd carried by alumina and aluminum silicate.

In the recently published investigation of Hettinger and co-workers [8] the formation of cyclopentanes from heptane was again observed in treatments over $Pt-Al_2O_3$ at 468° and 496° under hydrogen pressures of 5, 14, 24.5

and 35 atm. The authors state that under the conditions of their experiments the content of 1,2-dimethylcyclopentane in the heptane catalyzate is considerably greater than the ethylcyclopentane content. On this basis they conclude that 1,2-dimethylcyclopentane is formed as a result of the adsorption of heptane on the catalyst preferentially at the second and sixth carbon atoms. It seems to us that the possibility of the formation of ethylcyclopentane as a result of adsorption of heptane preferentially at the first and fifth carbon atoms is the same as in the case of adsorption at the second and sixth atoms. As regards the presence of more 1,2-dimethylcyclopentane in the catalyzate than ethylcyclopentane, this can probably be explained on the view that, under the conditions of the experiment, the ethylcyclopentane first formed is isomerized into 1,2-dimethylcyclopentane, as we have shown [1, 2] in a study of the transformations of ethylcyclopentane over Pt, Pd, and Rh supported by Al_2O_3 and SiO_2.

SUMMARY

1. The high-temperature catalytic transformations of n-heptane in a flow system in presence of Pt, Pd, and Rh supported on alumina and of hydrogen under pressure were investigated.

2. It was shown that, under the conditions used, the formation of aromatic hydrocarbons and isoparaffins was always accompanied by the dehydrocyclization of heptane with formation of a cyclopentane ring.

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Received October 18, 1956

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CATALYTIC HYDROGENOLYSIS OF FURAN COMPOUNDS

N. I. Shuikin and I. F. Bel'skii

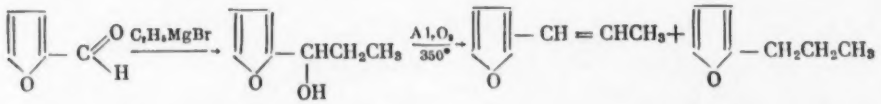
In previous investigations [1-3] we studied the hydrogenolysis of some 2-alkyl- and 2-alkenyl-furans in presence of Raney nickel in a flow system under ordinary pressure at various temperatures. It was then shown that 1) hydrogenolysis of the furan ring occurs both at C–O bonds and at C=C bonds; 2) the main direction in which the hydrogenolysis of the furan ring occurs consists in rupture of 1,5 C–O and "conjugated" rupture of 1,5 and 4,5 bonds, secondary alcohols and the corresponding ketones being formed; 3) the C–O bond adjacent to the side group undergoes hydrogenolysis only to a slight extent, but rupture of 2,3 C=C and 3,4 C–C is scarcely observed at all in any of the compounds investigated apart from 2-methylfuran; 4) the hydrogenolysis of alkenylfurans proceeds in the same way as that of alkylfurans; 5) rise in reaction temperature results in reduction in the content of alcohols in the products of the hydrogenolysis of the furan ring and a corresponding increase in the ketone content. With rise in temperature hydrogenolysis becomes predominant. Below 135-140° furan homologs can be smoothly converted into their tetrahydro derivatives; at 175° the extent of the hydrogenolysis of the furan ring in the compounds investigated attains 75-90%.

After consideration of all these results we hydrogenated mixtures of some 2-alkyl- and 2-alkenyl-furans at 235°. It would be expected that at this temperature complete scission of the furan ring would occur with formation of a more homogeneous hydrogenolysis product, i.e., ketones. This view was confirmed experimentally in this investigation. We obtained also a new result of some practical and theoretical significance. It was found that the 3,4 C–C bond is readily broken at 235°, whereas at a lower temperature (175°) no appreciable hydrogenolysis of this bond occurs.

EXPERIMENTAL

I. Hydrogenation of a Mixture of 2-Propyl- and 2-Propenyl-furans

2-Propyl- and 2-propenyl-furans were synthesized as follows:



α-Ethylfurfuryl alcohol was prepared by the Grignard reaction from 2-furaldehyde and ethyl bromide in yields of 75-80% on the furaldehyde taken; it had b.p. 74-75° (10 mm); d^{20}_4 1.0492; $n^{20}D$ 1.4886.

2-Propyl- and 2-propenyl-furans were prepared by the dehydration of α-ethylfurfuryl alcohol (300 g) over alumina at 350°. After being heated with sodium, the dehydration products were fractionated through a column of 30 theoretical plates; 40 g of 2-propylfuran and about 160 g of 2-propenylfuran were isolated.

2-Propylfuran had the following properties: b.p. 114-115° (745 mm); d^{20}_4 0.8876 and $n^{20}D$ 1.4395; found MR 32.67; calculated from $C_7H_{10}O$ MR 33.03. 2-Propenylfuran boiled at 132-133° (752 mm) and had d^{20}_4 0.9457; $n^{20}D$ 1.5098. Found MR 34.02; calculated for C_7H_8O MR 32.57.

A mixture (200 g) of 20% of 2-propylfuran and 80% of 2-propenylfuran was hydrogenated at 235° in presence of a Raney nickel catalyst prepared by the incomplete leaching of aluminum from a nickel-aluminum alloy. The hydrogenation was carried out at a rate of 0.06 $hour^{-1}$ in an excess of hydrogen. The catalyzate, which amounted

to 160 g after being dried with potassium carbonate, was fractionated through the 30-plate column. Narrow fractions isolated on the basis of the fractionation curve were identified by their physical properties and by the preparation of derivatives. The following compounds were isolated and identified (yield given in percent by weight on the catalyzate):

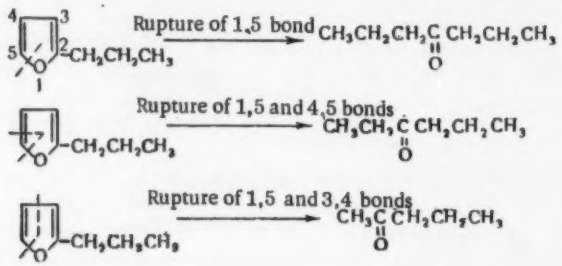
I. 2-Pentanone (41%): b.p. 100.4-101° (740 mm); d^{20}_4 0.8075; $n^{20}D$ 1.3911; found MR 25.34; calculated for $C_5H_{10}O$ MR 25.30. M.p. of semicarbazone 110.5°

II. 3-Hexanone (16%): b.p. 122-123° (740 mm); d^{20}_4 0.8195; $n^{20}D$ 1.4034; found MR 29.85; calculated for $C_6H_{12}O$ MR 29.92. M.p. of semicarbazone 109-110°.

III. 4-Heptanone (33%): b.p. 142.2-143° (743 mm); d^{20}_4 0.8176; $n^{20}D$ 1.4252; found MR 34.49; calculated for $C_7H_{14}O$ MR 34.53. M.p. of semicarbazone 131.5-132°.

IV. Heptyl alcohol (6%): b.p. 175-176° (750 mm); d^{20}_4 0.8228; $n^{20}D$ 1.4252; found MR 36.12; calculated for $C_7H_{16}O$ MR 36.05. The residue from the fractionation (about 4% of catalyzate), b.p. above 176°, was not investigated.

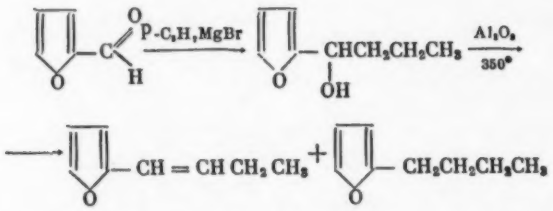
The results show that in the hydrogenation of a mixture of 2-propyl- and 2-propenyl-furans at 235° complete splitting of the ring occurs with formation of ketones as almost the sole hydrogenolysis products. In accordance with the scheme that we have assumed previously the formation of ketones by the hydrogenolysis of the furan ring can be represented as follows:



Heptyl alcohol could be otained by hydrogenolysis of the ring at 1,2 C—O. The small extent of hydrogenolysis of the furan ring at 1,2 C—O and the absence of rupture of 2,3 C—C indicates that the side group has a stabilizing action on neighboring bonds.

II. Hydrogenation of a Mixture of 2-Butyl- and 2-(1-Butenyl)-Furans

2-Butyl- and 2-(1-butenyl)-furans were prepared as follows:



α-Propylfurfuryl alcohol, prepared by the Grignard reaction from 2-furaldehyde and propyl bromide, had the following properties: b.p. 84-85° (8 mm); d^{20}_4 1.0391; $n^{20}D$ 1.4800. It was dehydrated over alumina at 350°. Fractionation of the dehydration products (185 g) through the 30-plate column gave 30 g of 2-butylfuran and 126 g of 2-(1-butenyl)furan.

2-Butylfuran had the following properties: b.p. 139.5-140.2° (750 mm); d^{20}_4 0.8877; $n^{20}D$ 1.4478; found MR 37.36; calculated for $C_8H_{12}O$ MR 37.65.

2-(1-Butenyl)furan boiled at 152-153° (750 mm) and had d^{20}_4 0.9288; $n^{20}D$ 1.5058; found MR 39.06; calculated for $C_8H_{10}O$ MR 37.18. A mixture of 30 g of 2-butylfuran and 126 g of 2-(1-butenyl)furan was hydrogenated at 235° over the same catalyst as that used for the hydrogenation of 2-propyl- and 2-propenyl-furans. The material was fed at a space velocity of 0.06 hour^{-1}. After being dried with potassium carbonate the catalyzate amounted to 122 g. As a result of fractionation of the catalyzate through the 30-plate column the following compounds were isolated and identified (yield given in percent by weight on catalyzate):

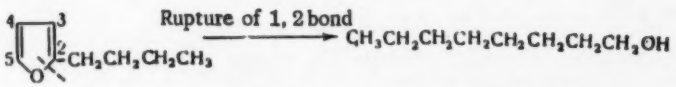
I. 2-Hexanone (42%): b.p. 126.3-126.5° (755 mm); d^{20}_4 0.8116; $n^{20}D$ 1.4015; found MR 30.01; calculated for $C_6H_{12}O$ MR 29.92. M. p. of semicarbazone 123-124°.

II. 3-Heptanone (16%): b.p. 146-146.2° (755 mm); d^{20}_4 0.8212; $n^{20}D$ 1.4112; found MR 34.53; calculated for $C_8H_{14}O$ MR 34.53. M. p. of semicarbazone 100-101°.

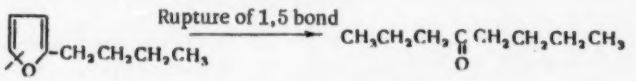
III. 4-Octanone (37%): b.p. 166.3-166.5° (757 mm); d^{20}_4 0.8190; $n^{20}D$ 1.4135; found MR 39.07; calculated for $C_8H_{16}O$ MR 39.15. M.p. of semicarbazone 94-95°.

IV. Octyl alcohol (3%): b.p. 194-195.5° (750 mm); d^{20}_4 0.8264; $n^{20}D$ 1.4302; found MR 40.72; calculated for $C_8H_{18}O$ MR 40.67. The residue (about 2% of catalyzate), b.p. above 196°, was not investigated.

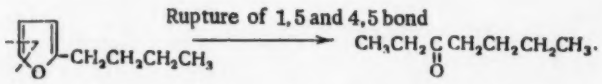
The results on the hydrogenation of 2-butyl- and 2-(1-butenyl)-furans at 235° show that complete hydrogenolysis of the furan ring occurs at this temperature with formation of ketones and a very small amount of octyl alcohol. The octyl alcohol could have been formed by splitting of the ring at the 1,2 C—O bond, adjacent to the side group:

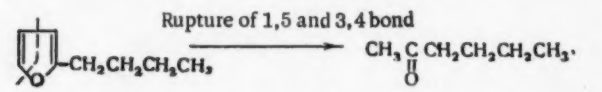


Hydrogenolysis of the ring at 1,5 C—O will lead to the formation of 4-octanone:



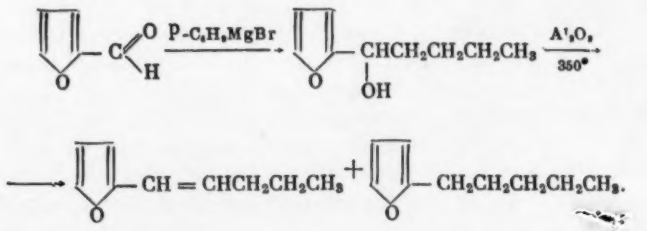
As in the preceding case, we assume that 2-hexanone and 3-heptanone are formed by "conjugated" hydrogenolysis of the ring at C—O and C—C bonds:





III. Hydrogenation of a Mixture of 2-Pentyl- and 2-(1-Pentenyl)-furans

2-Pentyl- and 2-(1-pentenyl)-furans were prepared as follows:



The conditions for the synthesis and the methods of purifying the products were the same as in the preceding cases. From 320 g of catalyzate obtained by the dehydration of α-butylfurfuryl alcohol we isolated 54 g of 2-pentylfuran and 210 g of 2-(1-pentenyl)furan by fraction through a column.

2-Pentylfuran had the following properties: b.p. 163.6-164° (745 mm); d^{20}_4 0.8835; $n^{20}D$ 1.4512; found MR 42.13; calculated for $C_9H_{14}O$ MR 42.27.

2-(1-Pentenyl)furan boiled at 60-60.5° (7 mm) and had d^{20}_4 0.9176; $n^{20}D$ 1.5006; found MR 43.7; calculated for $C_9H_{12}O$ MR 41.8.

We first carried out the hydrogenation of 2-(1-pentenyl)furan (60 g) at 235° in presence of the catalyst used in the preceding experiments. However, fractionation of the resulting catalyzate through a column gave about 40% of 2-pentylfuran, which indicated loss of catalytic activity in the course of the hydrogenolysis of the furan ring, though its hydrogenating power with respect to the olefin bond in the side chain was completely retained. For this reason we took a fresh portion of catalyst for the hydrogenation of the mixture of 2-pentyl- and 2-(1-pentenyl)--furans. The mixture (160 g), which contained about 25% of 2-pentylfuran, was hydrogenated at 235° at a space velocity of 0.06 $hour^{-1}$ in excess of hydrogen. The catalyzate contained a little water (not more than 5% on the weight of the catalyzate). After being dried with potassium carbonate it amounted to 125 g. By fractionation through a column we isolated and identified the following compounds (yield given in percent by weight on catalyzate):

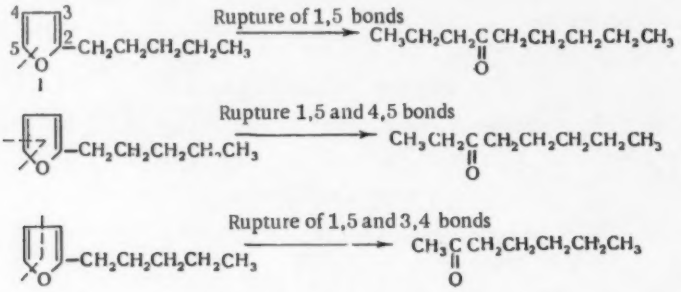
I. 2-Heptanone (45%): b.p. 149.8-150° (750 mm); d^{20}_4 0.8148; $n^{20}D$ 1.4095; found MR 34.68; calculated for $C_7H_{14}O$ MR 34.74. M. p. of semicarbazone 119.5-120°.

II. 3-Octanone (14%): b.p. 168-169° (740 mm); d^{20}_4 0.8243; $n^{20}D$ 1.4178; found MR 39.17; calculated for $C_8H_{16}O$ MR 39.16. M. p. of semicarbazone 92-93°.

III. 4-Nonanone (35%): b.p. 186-187° (740 mm); d^{20}_4 0.8236; $n^{20}D$ 1.4205; found MR 43.75; calculated for $C_9H_{18}O$ MR 43.77. M.p. of semicarbazone 85-86°.

The high-boiling part of the catalyzate (b.p. above 187°) was fractionated from a small flask fitted with a Vigreux column; the bulk of it came over at 213-215° and had d^{20}_4 0.8290; $n^{20}D$ 1.4330; found MR 45.22; calculated for $C_9H_{26}O$ MR 45.29. This part of the catalyzate, therefore, consisted mainly of nonyl alcohol.

As would be expected, the hydrogenolysis of 2-pentyl- and 2-(1-pentenyl)-furans at 235° proceeded in the direction of rupture of 1,5 C—O "conjugated" rupture of 1,5 and 3,4 and of 1,5 and 4, 5 bonds:



We carried out chromathermographic analysis of the gas obtained in the hydrogenation of 2-pentyl- and 2--(1-pentenyl)-furans at 235°. By analysis of the gas in the VTI apparatus it was established that it contained 1.8% of CO_2, 0.6% of unsaturated hydrocarbons, and quantities of hydrogen and saturated hydrocarbons. By chromathermoanalysis we determined the relative contents of saturated hydrocarbons in the gas: methane (3%), ethane (18%), propane (8%), and butane (71%) (the total amount of saturated hydrocarbons being taken as 100%). We consider that the results of the chromathermographic analysis of the gas provide new evidence in confirmation of our proposed mechanism for the formation of products of the hydrogenolysis of the furan ring. The fact that the saturated hydrocarbons consisted mainly of butane provides grounds for the view that the primary act of the hydrogenolysis of the ring yields radicals which, by undergoing recombination and hydrogenation, can give more complex molecules. If this view is correct, then "conjugated" hydrogenolysis of the 1,5 and 4,5 bonds should give not only the corresponding ketone (or alcohol), but also a C_1 radical; and "conjugated" rupture of the 1,5 and 3,4 bonds should give a C_2

radical. Since the furan ring is split predominantly at the 1,5 and 3,4 bonds at 235°, the concentration of C_2 radicals at the catalyst surface should be very high. The hydrogenation of these radicals or their combination among themselves should give ethane or butane, respectively. Analysis showed that the gas formed in the reaction did indeed consist mainly of butane and ethane. The relative contents of ethane and butane in the gas show that, of the two reactions (hydrogenation and recombination) into which the C_2 radical may enter, the second is predominant.

The C_1 radical may either be hydrogenated to methane or recombined (with a like radical with formation of ethane, or with a C_2 radical with formation of propane). The recombination of C_1 and C_2 radicals with formation of propane must be the most probable because of the higher concentration of C_2 radicals at the catalyst surface.

* * *

As we have shown previously [1-3], the hydrogenolysis of 2-methylfuran at 200° and of 2-ethyl-, 2-propenyl-, 2-isobutyl-, 2-isobutenyl-, and 2-pentenyl-furans at 175° proceeds mainly in the direction of scission of the furan ring at 1,5 C—O and 4,5 C—C. Scarcely any rupture of 3,4 C—C bonds occurs at this temperature. The extent of the hydrogenolysis of the furan ring in these compounds (apart from 2-ethylfuran) is 75-90%. The results of the present investigation show that in the hydrogenolysis of 2-propyl-, 2-butyl-, and 2-pentyl-furans at 235° scission of the ring goes to completion with formation of ketones and very small amounts of primary alcohols. Of the ketones, the greatest amount is formed of those in which the keto group is in the second or fourth position (2-pentanone, 2-hexanone, 2-heptanone, and also 4-heptanone, 4-octanone, and 4-nonanone). Thus, whereas the hydrogenolysis of the furan ring at 175° proceeds mainly in the direction of rupture of 1,5 C—O and "conjugated" rupture of the 1,5 and 4,5 bonds, with rise in the hydrogenation temperature to 235°, the main direction of the hydrogenolysis of the ring becomes "conjugated" rupture of the 1,5 and 3,4 bonds and rupture of the 1,5 C—O bond. This result shows that the susceptibility of the various bonds of the furan ring to hydrogenolysis is a function of the temperature. At the lower temperature 1,5 C—O and 4,5 C=C are most readily broken, whereas 3,4 C—C is scarcely touched. At the higher temperature, on the other hand, 3,4 C—C is most readily hydrogenolyzed, and the 4,5 C=C bond is more stable.

We must draw attention to the following fact: the relative contents of ketones of the various structures in the products of hydrogenolysis of the investigated compounds remain almost constant and are independent of the length of the side chain. In the hydrogenation of 2-propyl-, 2-butyl-, and 2-pentyl-furans, 41-45% of ketones with the keto group in the 2-position, 14-16% of ketones with the keto group in the 3-position, and 33-37% of ketones with the keto group in the 4-position are formed. Hence, the relative resistances to hydrogenolysis of the 1,5 C—O bond, the 4-4 C=C bond, and the 3-4 C—C bond are independent of the length of the side chain under given hydrogenation conditions.

The absence of alcohols or ketones formed by the rupture of the 2,3 C=C bond among the hydrogenolysis products, and also the smallness of the amount of primary alcohols formed by hydrogenolysis of the ring at 1,2 C—O, shows that the side group has a stabilizing effect on the adjacent C—O and C=C bonds. We found that, when the catalyst had been used for the hydrogenation of 2-propyl- and 2-butyl-furans, it lost much of its activity with respect to the hydrogenolysis of the furan ring, but fully maintained its hydrogenating ability with respect to a double bond in the side chain. This fact is probably to be explained on the view that hydrogenation of an ethylenic bond in the side chain and hydrogenolysis of the furan ring proceed at different active centers.

SUMMARY

1. It was shown that the hydrogenation of 2-propyl-, 2-butyl-, and 2-pentyl-furans at 235° in a flow system at ordinary pressure in presence of Raney nickel leads to the complete scission of the furan ring with formation of aliphatic ketones and a very small amount of primary alcohols.

2. It was shown that the furan ring in these compounds is hydrogenolyzed with rupture of the 1,5 C—O bond, and also with "conjugated" rupture of the 1,5 and 4,5 bonds and of the 1,5 and 3,4 bonds.

3. It was found that the relative stabilities of the different bonds in the furan rings of 2-propyl-, 2-butyl-, and 2-pentyl-furans are independent of the length of the side chain.

4. Some results were obtained which support the view that the hydrogenolysis of the furan ring proceeds by a free-radical mechanism.

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Received October 27, 1956

*Original Russian pagination. See C. B. Translation.

CONTACT-CATALYTIC DEHYDROCYCLIZATION OF PIPERYLENE

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Quite inadequate attention has been given to the catalytic reactions of aliphatic dienes. This applies in particular to piperylene, the investigation of which is of special interest in view of the presence of geometric isomerism and of mobile hydrogen atoms in this compound, as distinct from butadiene and isoprene. Sources of piperylene are to be found in cracking gases, wastes from the synthetic rubber industry, and particularly 2-furaldehyde, which is a by-product of the manufacture of wood-hydrolysis alcohol.

The study of the dehydrocyclization of piperlylene with formation of cyclopentadiene, a compound of some importance in organic synthesis, presented considerable interest. The replaceability of a methylene hydrogen in cyclopentadiene bya metal of the MgBr group makes it possible to carry out all reactions characteristic for organometallic compounds with cyclopentadiene substituted in this way. The use of cyclopentadiene in the diene synthesis opened the way to the preparation of many bicycloheptene derivatives. By the condensation of cyclopentadiene with carbonyl compounds we can obtain fulvenes, which are themselves extremely reactive compounds. Cyclopentadiene compounds of the fulvene type [1], like cyclopentane (which is readily obtained by the hydrogenation of cyclopentadiene), may be used as additives to fuels for internal combustion engines because of their good antidetonation characteristics. From cyclopentadiene highly effective insecticides, such as "chlordan" and "aldrin", can be prepared. Also, cyclopentadiene gives copolymers [2] with butadiene, isoprene, piperylene, 1-buten-3-yne, and other unsaturated hydrocarbons and so yields new improved synthetic rubbers and valuable resins.

The catalytic transformations of piperylene and its dimer were studied by Rachinskii, Zal'manovich, and Tsiper [3], who showed that in the passage of piperylene over gumbrin at 270° formation of the dimer was accompanied by that of 2-pentene, which was formed as a result of redistribution of hydrogen. An indication that the dehydrocyclization of piperylene can occur is found in a paper by Kennedy and Hetzel [4], who in the treatment of piperylene in presence of an alumina-chromia catalyst obtained a condensate containing about 9% of cyclopentadiene. These authors considered that the dehydrocyclization of piperylene was noncatalytic; they studied the transformations of piperylene in presence of various aluminum silicate catalysts, but they did not make a full analysis of the transformation products. The thermal transformations of piperylene were later studied by us [5]; we showed that in the treatment of piperylene in contact with noncatalyzing material (crushed quartz) the yield of cyclopentadiene was only 1% in experiments at 600°, which throws doubt on Kennedy and Hetzel's conclusions concerning the noncatalytic character of the dehydrocyclization of piperylene. In view of this we considered that it would be of interest to make a more detailed study of the dehydrocyclization of piperylene in presence of various catalysts.

As a result of our investigation it was found, in confirmation of the views previously expressed by one of us [6], that the reaction is catalytic and the yields of cyclopentadiene are greatly dependent on the nature of the catalyst. We investigated several catalysts, of which the most effective were alumina-chromia promoted with potassium oxide and platinized charcoal (5% Pt). The maximum yield of cyclopentadiene, obtained by recyclization of unchanged piperylene, can attain 40%. We studied also the composition of the products of the transformation of piperylene; it was then found that at reduced pressure (20 mm) there occurred dehydrocyclization, isomerization, hydrogenation, cracking and condensation with formation of highly condensed compounds that formed a carbonaceous deposit on the catalyst. It was found that at atmospheric pressure, apart from these reactions, transformations occurred with formation of a considerable amount of aromatic hydrocarbons: benzene (26.5%) and toluene (15%). It is probable that these hydrocarbons were formed by dehydrogenation and dealkylation of the piperylene dimer, which is readily formed at elevated temperatures [3]. However, under reduced pressure the formation of the dimer and its transformation products was prevented almost completely.

EXPERIMENTAL

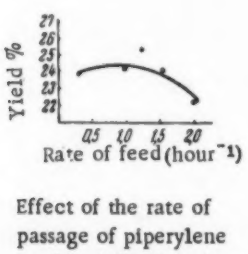
Piperylene (b.p. 42-43°; $n^{20}D$ 1.4320 and d^{20}_4 0.6830), consisting of a mixture of cis and trans forms in equal amounts, was brought into contact with the catalysts listed in Table 1 at 500-650° in a quartz tube of diameter 18 mm. The treatment was carried out on 50-ml portions (34.2 g) under reduced (20 mm) and atmospheric pressures, and also in presence of nitrogen as diluent.

TABLE 1

Results of Experiments on the Dehydrocylization of Piperylene at 600° Under Reduced Pressure (20 mm).

Experiment	Catalyst (with molar proportions of components)	Space velocity (hour^{-1})	Cyclopentadiene cont. of catalyzate (%)	Yield of liquid catalyzate (%)	Yield of cyclopentadiene (%)	Coke formation (% by weight)
1	5% Pt-charcoal	0,4	20,0	89,1	18,4	—
2	Activated charcoal	0,4	4,3	92,2	4,2	—
3	1% Pt-pumice	1,5	16,0	92,4	15,3	4,1
4	Pumice	1,5	4,5	95,1	4,4	2,5
5	$Cr_2O_3 + Al_2O_3 + K_2O$ (7 : 42 : 1)	0,5	25,0	72,5	18,6	17,1
6	$Cr_2O_3 + Al_2O_3$ (1 : 4)	1,0	12,8	76,3	10,1	12,3
7	Cr_2O_3 + pumice + K_2O (7 : 42 : 1)	0,6	9,0	93,1	8,7	4,2
8	$Cr_2O_3 + TiO_2 + K_2O$ (7 : 42 : 1)	0,6	4,5	85,2	3,9	6,1
9	$Cr_2O_3 + TiO_2 + ZnO + K_2O$ (7 : 17 : : 25 : 1)	0,6	3,5	83,0	3,0	7,2
10	$MoO_2 + Al_2O_3$ (1 : 4)	0,8	16,4	66,4	11,1	12,3
11	$MoO_2 + Al_2O_3 + ZnO$ (1 : 4 : 5)	0,6	6,2	78,0	5,1	8,5
12	$TiO_2 + Al_2O_3$ (1 : 1)	0,6	3,8	80,2	3,3	6,2
13	$ZnO + Al_2O_3$ (1 : 1)	0,6	3,1	88,1	2,8	5,0
14	$ZrO_2 + Al_2O_3$ (1 : 1)	0,6	3,0	76,4	2,4	14,2
15	$ThO_2 + Al_2O_3$ (1 : 20)	0,6	3,4	82,0	2,9	7,0
16	Pumice Al_2O_3	1,2	3,5	77,8	2,8	8,3

The most effective catalysts, $Al_2O_3 + Cr_2O_3 + K_2O$ (84 : 14 : 2 moles %) and 5% Pt-charcoal, were prepared as follows. The alumina-chromia-potassia catalyst was prepared by the method of Shuikin, Dobryna, and Timofeeva [7] by impregnation of activated alumina with potassium and ammonium dichromate solutions and subsequent decomposition. The specific surface of this catalyst, determined by the dynamic method from a single point on the curve, was 97.9 sq.m/g; pH 6.7. In the preparation of platinized charcoal, the charcoal was first impregnated with a solution of chloroplatinic acid, which was reduced with formaldehyde and alkali under cooling. Apart from platinized charcoal, the catalysts were regenerated by treatment with air for four hours at the temperature of the experiment after every three experiments.



Effect of the rate of passage of piperylene on the yield of cyclopentadiene.

The cyclopentadiene contents of the catalyzates were determined by Afanas'ev's method [8], and the catalyzates were then subjected to precision fractionation, the individual fractions being investigated chemically and with the aid of Raman spectra. The composition of gaseous products was determined in an Orsat-Lunge apparatus; the gas was analyzed in greater detail by the chromathermographic method [9]. The extent of coke formation on the catalyst was determined from the difference in weight of the catalyst before and after the experiment.

Dehydrocyclization of Piperylene. The results of typical experiments on the dehydrocyclization of piperylene in presence of various catalysts at 600° under reduced pressure (20 mm) are given in Table 1. Table 1 shows that the best results were obtained in the passage of piperylene over alumina-chromia-potassia catalyst and over platinized charcoal; in these experiments the yields of cyclopentadiene obtained in one passage were 25% and 20% respectively. A somewhat lower yield of cyclopentadiene (16.4%) was obtained with an alumina-

-molybdia catalyst. Eighty experiments were carried out with the alumina-chromia-potassia catalyst (duration of each experiment about one hour), and its activity remained at the initial value. It was noted that the yield of liquid catalyzate increased as the amount of work done by the catalyst increased.

Table 1 shows also that the course of the dehydrocyclization reaction depends both on the composition of the catalyst and on the nature of the carrier. Thus, with a chromia-potassia catalyst on pumice (Experiment 7) only slight cracking occurs, the yield of liquid catalyzate is high, but the extent of conversion into cyclopentadiene is very low. With the same catalyst supported by alumina (Experiment 5) the yield of cyclopentadiene is considerably higher, but the yield of liquid products is lower as a result of increased cracking. Hence, the high cracking power of the alumina-chromia-potassia catalyst is due mainly to the presence of alumina; this is confirmed also by Experiment 16, in which pure alumina was used.

In the study of the dehydrocyclization of piperylene we determined also the effect of temperature and rate of passage of piperylene. The results of experiments on the dependence of the yield of cyclopentadiene on temperature at 20 mm are shown in Table 2.

TABLE 2

Effect of Temperature on the Dehydrocyclization of Piperylene at 20 mm

Catalyst	Temperature (°C)	Yield of liquid catalyzate (%)	Yield of cyclopentadiene (%)	
			on the catalyzate	on the orig. piperylene
$Al_2O_3 + Cr_2O_3 + K_2O$	500	85	11	9,3
Ditto	550	82	13	10,6
»	575	79	17	13,4
»	600	72	25	18,0
»	625	65	25	16,6
»	650	59	27	15,9
5% Pt-charcoal	550	96	14	13,4
Ditto	600	94	20	18,8
»	625	90	21	18,9

Table 2 shows that the optimum temperature for the dehydrocyclization of piperylene is 600°.

The results of experiments on the effect of the rate of feed of piperylene into the reaction zone on the yield of cyclopentadiene in presence of the alumina-chromia-potassia catalyst at 600° are shown in the figure.

The figure shows that change in space velocity of piperylene in the range 0.3-1.5 hour^{-1} has no substantial effect on the yield of cyclopentadiene, whereas increase in the space velocity above 1.5 hour^{-1} results in a considerable fall in yield.

In order to determine the effect of pressure on the character and extent of the transformations of piperylene, experiments were carried out on its dehydrocyclization at atmospheric pressure and in a stream of nitrogen (4 : 1 molar dilution with nitrogen) in presence of various catalysts. The results are given in Table 3.

Table 3 shows that the cyclopentadiene contents of catalyzates obtained at atmospheric pressure are lower than in the dehydrocyclization of piperylene at 20 mm (Table 1). Dilution with nitrogen did not result in increased yield of cyclopentadiene; moreover, the yield of condensate was less.

The fractional composition of some typical catalyzates obtained in the treatment of piperylene with an alumina-chromia-potassia catalyst at reduced (20 mm) and atmospheric pressures and also in presence of nitrogen as diluent are given in Table 4.

Fraction I consisted mainly of 1-pentene, 2-methyl-1-butene (the presence of the hydrocarbons was proved by the Raman spectrum method), and 1,4-pentadiene (the presence of this was proved by the isolation of 1,2,4,5-tetrabromopentane, b.p. 163-165° (12 mm) and m.p. 85°, after the bromination of the fraction). Spectrum analysis

indicated that Fraction II consisted of a mixture of trans-2-pentene, 2-methyl-1-butene, and isoprene, the presence of which was confirmed by the preparation of its adduct with maleic anhydride (m.p. 63°) [10]. Fractions III and IV consisted of cyclopentadiene and unchanged piperylene. Fractions V-IX contained benzene (V and VI), toluene (VII and VIII), ethylbenzene (IX), and m- and p-xylenes, the presence of which was proved by spectrum analysis and Ullmann oxidation [11]. By the oxidation of the hydrocarbons of Fraction IX we obtained benzoic acid (m.p. 120°) and iso- and tere-phthalic acids (m.p. of dimethyl esters 64° and 138°). In addition to aromatic hydrocarbons the higher-boiling fractions contained olefins, e.g., 2-hexene, 3-hexene, and 3-methyl-1,3-pentadiene. Fraction X consisted mainly of naphthalene, which melted at 79.5° after recrystallization from alcohol. The presence of naphthalene in this fraction was confirmed by measurement of the ultraviolet spectrum.

TABLE 3

Dehydrocyclization of Piperylene at 600° at a Space Velocity of 0.8 hour^{-1} under Atmospheric Pressure and in Presence of Nitrogen as Diluent

Catalyst	Pressure	Yield of catalyzate (%)	$n^{20}D$ of catalyzate	Cyclopentadiene content of catalyzate	Amount of gas liberated (liters at STP)	Coke formation (%)
$Al_2O_3 + Cr_2O_3 + K_2O$	Atmospheric	59	1,5020	16,0	16	21
5% Pt-charcoal	»	89	1,4675	18,0	10	—
1% Pt-pumice	»	90	1,4660	2,8	5	6
Al_2O_3	»	62	1,4870	1,3	14	10
$Al_2O_3 + Cr_2O_3 + K_2O$	Diluted with N	52	1,4630	15,0	—	13
5% Pt-charcoal	»	78	1,4575	14,0	—	—

TABLE 4

Fractional Compositions of Piperylene Catalyzates Obtained at Atmospheric and Reduced (20 mm) Pressures and in Presence of Nitrogen as Diluent (4 : 1 molar ratio) (Experiments at 600°).

Fraction	Boiling range (°C, corrected)	Yield of fraction, %			Properties of fract.*		Results of chemical and Raman analyses**
		at 20 mm	at atm. pressure	diluted with nitrogen	n_D^{20}	d_4^{20}	
I	26—32	4,2	4,8	4,6	1,3825	0,6588	1-Pentene (mainly), 2-methyl--1-butene, 1,4-pentadiene
II	32—37	4,0	6,3	5,6	1,3970	0,6647	trans-2-Pentene, 2-methyl-1--butene, isoprene
III	37—41	4,4	4,7	4,4	1,4310	0,6825	Cyclopentadiene and trans--piperylene
IV	41—45	82,4	22,5	45,5	1,4368	0,6858	Cyclopentadiene, cis- and trans--piperylenes in equal amounts
V	45—75	—	2,7	3,5	1,4470	0,7470	Predominantly (about 95%) benzene, 2-hexene, 3-hexene, and 3-methyl-1,3-pentadiene
VI	75—98	—	25,3	15,7	1,4975	0,8635	
VII	98—112	—	10,7	9,0	1,4915	0,8590	Toluene (95%) with some olefins
VIII	112—125	—	5,0	4,0	1,4780	0,8550	
IX	125—150	—	4,0	1,7	1,5055	0,8620	Ethylbenzene, m- and p-xylenes
X	150—210	—	6,7	1,0	—	—	Naphthalene
	Residue	3,6	5,6	4,5	—	—	—
	Losses	1,4	1,7	1,5	—	—	—

The three fractions boiling within the same limits were analyzed separately; their properties were almost the same and their compositions were identical; they are treated as identical in the table.

** The Raman spectrum analysis was carried out by Iu. P. Egorov, to whom we express our thanks.

It is noteworthy that the composition of the catalyzate is to a great extent dependent on the pressure at which the catalytic treatment is carried out. Thus, at reduced pressure only a small amount of the pentene-isoprene part of the catalyzate was formed and scarcely any of the aromatic part (apart from cyclopentadiene dimer, only traces of benzene and toluene were found in the residue). Most of the condensate was unchanged piperylene, which was contained in the piperylene-cyclopentadiene fraction, the content of which was 82.4%. At atmospheric pressure a large amount of aromatic hydrocarbons was formed: about 26.5% of benzene and about 15% of toluene; the content of the piperylene-cyclopentadiene fraction was only 22.5%. When the piperylene was diluted with nitrogen, aromatic hydrocarbons were again formed, though in smaller amount, while there was more unchanged piperylene than in the reaction at atmospheric pressure.

TABLE 5

Composition of the Gaseous Products of the Catalytic Dehydrocyclization of Piperylene

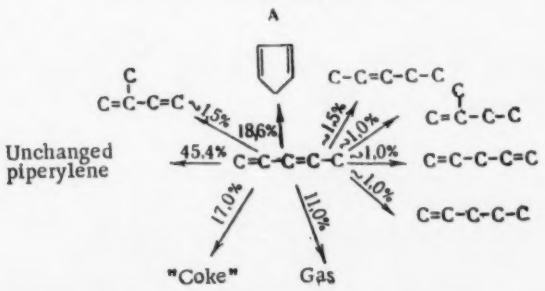
Temperature (°C)	Catalyst	Group composition		Individual composition								
		C_nH_{2n}	C_nH_{2n+2}	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8	C_4H_6
600	Pt-charcoal	18	45	37	17	9	8	10	—	5	6	8
600	Pt-pumice	44	39	17	16	17	11	3	22	5	4	5
600	$Al_2O_3+Cr_2O_3+$ $+K_2O$	21	29	50	9	10	7	5	7	3	—	9
500	Ditto	32	30	58	8	15	4	8	7	5	8	7

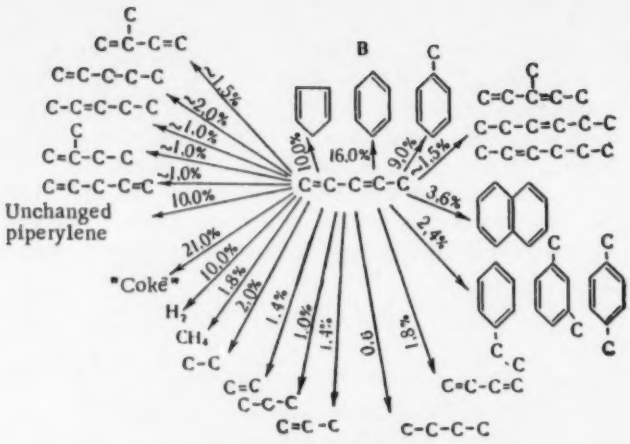
Hence, at reduced pressure side reactions are strongly suppressed, which makes it possible to re-utilize a large amount of unchanged piperylene.

Analysis of Gaseous Products. When the group composition of the gas had been determined and the butadiene content found by analysis in a Bushmarin apparatus [12], the gas mixture was investigated in detail by the chromathermographic method [9]. The results on the composition of gaseous products obtained by the treatment of piperylene in presence of platinized charcoal, platinized pumice, and the alumina-chromia-potassia catalyst are given in Table 5.

Table 5 shows that in the catalytic treatment of piperylene a mixture of various C_1-C_4 gaseous hydrocarbons is formed with a predominance of methane and ethane. The formation of saturated hydrocarbons probably occurs as a result of the hydrogenation of molecule fragments by hydrogen liberated in the dehydrocyclization of piperylene. The hydrogen content of the gas mixture obtained in presence of the alumina-chromia-potassia catalyst is considerably greater than that of the gas mixture obtained in presence of a platinum catalyst. The high content of saturated hydrocarbons obtained in presence of a platinum catalyst is to be explained by the fact that hydrogenation proceeds much more readily in presence of platinum than in presence of oxide catalysts. Hence, as a result of the catalytic transformations of piperylene a complex mixture of hydrocarbons is formed consisting of products of dehydrocyclization, isomerization, hydrogenation, methylation, and dimerization with subsequnet dehydrogenation and dealkylation of the cyclic dimer.

An important factor affecting the character of the transformations of piperylene is pressure. The compositions of the products formed in presence of an alumina-chromia-potassia catalyst under reduced pressure (A) and under atmospheric pressure (B) may be represented diagrammatically as follows:





SUMMARY

1. An investigation was made of the dehydrocyclization of piperylene in presence of various catalysts at reduced and ordinary pressures. This reaction gives the highest yields of cyclopentadiene (18.6-18.4%) in presence of alumina-chromia-potassia and platinized charcoal catalysts.

2. The results confirm the view that the dehydrocyclization of piperylene is catalytic in character.

3. The effects of temperature, pressure, and rate of passage of piperylene on the yield of cyclopentadiene were studied; the optimum conditions for its formation were determined.

4. A scheme of analysis was developed for the complex mixture of products of the catalytic dehydrocyclization of piperylene.

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Received November 3, 1956

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DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF GASOLINES FROM TATARIIA PETROLEUMS

COMMUNICATION 2. GASOLINE FROM ROMASHKIN PETROLEUM (MINNIBAEV AREA)

F. A. Urmancheev, E. A. Robinzon, S.-Kh. G. Kashaev, and B. Le

In our first communication [1] we described the individual hydrocarbon composition of gasolines of upper boiling limit 150° from Bavlin and Romashkin petroleums. In the present paper we report results on the gasoline from Innibaev petroleum.

EXPERIMENTAL

The gasoline for investigation was separated from Minnibaev petroleum, which was collected in 1953 from the second stratum of the first devonian horizon D_1^2 (Well No. 53); depth of origin 1750.5-1762 m. This petroleum has the following properties: d^{20}_4 0.8570, paraffin content 3.3* -3.5%**, resins (acidic) 30.8%, sulfur 1.43%***.

Minnibaev gasoline was investigated by the combined method developed by Kazanskii and Landsberg [2] and used by us in the investigation cited above [1]. On the basis of our investigation we have calculated the contents of paraffin, cyclopentane, cyclohexane, and aromatic hydrocarbons. The contents of all the hydrocarbons found in the gasoline are expressed as percent by weight of the "whole" gasoline, i.e., on the wide fraction boiling up to 150° (which will be denoted by W). Our results are summarized in Table 1, in which we give also the quantitative balance sheet for the whole investigation.

Table 1 shows that the Minnibaev gasoline was accounted for in the analysis to the extent of 84.6%; 66 hydrocarbons were found in it. The distribution of these hydrocarbons over the various classes, with separate consideration of normal and branched paraffins and also of cyclopentanes and cyclohexanes, is shown in Table 2.

It follows from Tables 1 and 2 that Minnibaev gasoline is predominantly paraffin in composition and, like Bavlin and Romashkin gasolines, is close in composition to Tuimazin petroleum [3], which contains 66.2% of paraffins, 16.5% of naphthenes, and 5.2% of aromatic hydrocarbons. Minnibaev gasoline, like Romashkin, contains approximately equal amounts of normal and branched paraffins. The branched paraffins in Minnibaev gasoline, like those in other gasolines investigated, consist mainly of hydrocarbons containing a tertiary carbon atom; the content of paraffins having a quaternary carbon atom is very small indeed (less than 1%). A characteristic of Minnibaev gasoline, which distinguishes it from Tuimazin gasoline [3], is the presence among the isoparaffins of hydrocarbons containing two or even three tertiary carbon atoms in the molecule (2,3,5-trimethylhexane); these hydrocarbons were not detected in Tuimazin gasoline.

Examining the groups of isomeric paraffins, we find that all possible C_5 and C_6 paraffins were detected, except neopentane. All C_7 isomers were found except 2,2,3-trimethylbutane and 3,3-dimethylpentane, i.e., hydrocarbons having a quaternary carbon atom. Of C_8 hydrocarbons we found octane, all three methylheptanes, and

* Determined by the destructive-fractionation method.

** Determined by the adsorption method.

*** According to results from the Laboratory of Petroleum Chemistry, Chemical Institute of the Kazan Affiliated Body of the Academy of Sciences of the USSR.

TABLE 1

Individual Hydrocarbons Found in Minnibaev Gasoline

Hydrocarbon	Content (% by weight on whole gasoline W)	Hydrocarbon	Content (% by weight on whole gasoline W)
Paraffins			
Propane	1.74	2,4-Dimethylpentane	0.12
Butane	6.06	3-Ethylpentane	0.31
Isobutane	5.36	Octane	5.93
Pentane	5.37	2-Methylheptane	3.38
2-Methylbutane	2.95	3-Methylheptane	0.89
Hexane	5.18	4-Methylheptane	1.00
2-Methylpentane	3.61	2,3-Dimethylhexane	0.60
3-Methylpentane	2.88	2,4-Dimethylhexane	0.59
2,2-Dimethylbutane	0.03	Nonane	1.49
2,3-Dimethylbutane	0.25	2-Methyloctane	0.86
Heptane	6.50	3-Methyloctane	0.91
2-Methylhexane	1.98	4-Methyloctane	0.56
3-Methylhexane	3.46	2,3,5-Trimethylhexane	0.27
2,2-Dimethylpentane	0.12	2,6-Dimethylheptane	0.68
2,3-Dimethylpentane	0.75		
		Total	63.85
Cyclopentane Hydrocarbons			
Cyclopentane	0.40	cis-1,2,3-Trimethylcyclopentane	0.10
Methylcyclopentane	1.39	1-cis-2-trans-3-cis-Trimethylcyclopentane	0.39
cis-1,2-Dimethylcyclopentane	0.32	1-cis-2-trans-4-cis-Trimethylcyclopentane	0.39
trans-1,2-Dimethylcyclopentane	0.87	1,2-cis-4-trans-Trimethylcyclopentane	0.30
cis-1,3-Dimethylcyclopentane	0.65	1-Methyl-3-propylcyclopentane	0.15
trans-1,3-Dimethylcyclopentane	0.52	Propylcyclopentane	0.39
Ethylcyclopentane	0.59	Isopropylcyclopentane	0.23
		Total	6.69
Cyclohexane Hydrocarbons			
Cyclohexane	1.09	1-Ethyl-2-methylcyclohexane	0.08
Methylcyclohexane	3.34	1-Ethyl-3-methylcyclohexane	0.17
1,1-Dimethylcyclohexane	0.22	1-Ethyl-4-methylcyclohexane	0.08
1,2-Dimethylcyclohexane	0.35	1,1,2-Trimethylcyclohexane	0.15
1,3-Dimethylcyclohexane	0.98	1,1,3-Trimethylcyclohexane	1.39
1,4-Dimethylcyclohexane	0.43	1,1,4-Trimethylcyclohexane	+*
Ethylcyclohexane	0.83		
Propylcyclohexane	0.07	1,2,4-Trimethylcyclohexane	0.10
Isopropylcyclohexane	0.06	1,3,5-Trimethylcyclohexane	0.06
		Total	9.40
Aromatic Hydrocarbons			
Benzene	0.64	Accounted for (%)	84.65
Toluene	1.73	Unaccounted for (%)	4.59
Ethylbenzene	0.82	Residues from Fractionations (%)	3.32
o-Xylene	0.23	Losses (%)	7.44
m-Xylene	0.94		
p-Xylene	0.35		
Total	4.71		

*The sign + indicates that the hydrocarbon was detected only qualitatively.

2,3- and 2,4-dimethylhexanes. Of C_9 hydrocarbons we found nonane, all three methyloctanes, 2,6-dimethylheptane, and 2,3,5-trimethylhexane. No still more highly branched hydrocarbons of the C_8 and C_9 groups were detected.

TABLE 2

Distribution of the Hydrocarbons Found According to Classes

Class of hydrocarbons	No. of such hydrocarbons found in the gasoline	Content (% by weight)
Normal paraffins	7	32,27
Paraffins containing a tertiary carbon	20	31,43
Paraffins containing a quaternary carbon	2	0,15
Cyclopentanes	14	6,69
Cyclohexanes	17	9,40
Aromatics	6	4,71
Total	66	

Of the cyclopentane hydrocarbons the highest content was found for methylcyclopentane (1.39% on W); of C_7 cyclopentane hydrocarbons all were detected except 1,1-dimethylcyclopentane. Of the cyclohexane hydrocarbons methylcyclohexane was present in the greatest amount (3.34% on W). Among C_8 hydrocarbons 1,3-dimethylcyclohexane and ethylcyclohexane were present in the greatest amount; among the ethylmethylcyclohexanes the 1,3-isomer predominated; and of the trimethylcyclohexanes 1,1,3-trimethylcyclohexane with a quaternary carbon atom was present in the largest amount. All possible aromatic hydrocarbons were found; toluene was present in the greatest amount; among the C_8 hydrocarbons m-xylene and ethylbenzene predominated.

TABLE 3

Comparative Table of the Contents of Certain Hydrocarbons in Gasolines*

Hydrocarbon	Content (% by weight)				Content (% by volume)
	Bavlin	Romashkin	Minnibaev	Tuimazin	Bradford
Hexane	6,71	5,41	5,18	8,43	6,31
Heptane	7,98	6,79	6,50	9,74	7,71
Cyclopentane	0,43	0,28	0,40	0,37	0,23
Methylcyclopentane	1,83	1,56	1,39	2,44	1,50
Cyclohexane	1,27	1,04	1,09	1,21	1,95
Methylcyclohexane	3,07	2,88	3,34	3,74	6,27
Benzene	0,67	0,44	0,64	0,53	0,19
Toluene	1,70	1,12	1,73	1,85	1,52

* The data on Bradford gasoline refer to the 40-180° fraction; the data on the Tatar and Tuimazin gasolines refer to a fraction of boiling limit 150°.

Hence, with respect to its over-all contents of paraffin, naphthene, and aromatic hydrocarbons Minnibaev gasoline was similar to bavlin and Romashkin gasolines; with respect to its approximately equal contents of normal and branched paraffins it was similar to Romanshkin gasoline.

It is interesting to compare the gasolines from Tatar gasolines with gasolines from other paraffin-base petroleums: Tuimazin [3] (Bashkiriia) and Bradford [4] (Pennsylvania, US). For comparsion purposes we have taken certain paraffin, naphthene, and aromatic hydrocarbons which, with the exception of cyclopentane, cyclohexane, and benzene, are present in these gasolines in considerable amounts. Data for comparison are given in Table 3.

Table 3 shows that Tatar gasolines have lower hexane, pentane, and methylcyclopentane contents than Tuimazin gasoline. Comparison of the gasolines that we have investigated with Bradford gasoline indicates that in the former the methylcyclohexane content is somewhat lower and the benzene content is somewhat higher. Table 3 shows also that the relative amounts of the homologs in the pairs shown (heptane and hexane, methylcyclopentane and cyclopentane, methylcyclohexane and cyclohexane, toluene and benzene) are roughly the same for all the gasolines examined.

The chemical part of the investigation was carried out in the Laboratory of Petroleum Chemistry of the A. E. Arbuzov Chemical Institute of the Kazan Affiliated Body of the Academy of Sciences of the USSR. The Raman spectrum investigation was carried out in the Laboratory of Physicochemical Methods of Investigation of the Kazan Affiliated Body of the Academy of Sciences of the USSR. The analysis of gases for the contents of individual hydrocarbons was carried out by L. M. Mukhamedova with an apparatus of the TsIATIM-51 type.

SUMMARY

1. It was shown that Minnibaev, Bavlin, and Romashkin gasolines, which originate from coeval devonian petroleums, are close in individual hydrocarbon composition.

2. Minnibaev and Romashkin gasolines, being derived from petroleums of the same Romashkin depost, are similar with respect to the approximate equality of the contents of normal and branched paraffins; in this respect they differ from Bavlin and Tuimazin petroleums, in which normal paraffins predominate to some extent over isoparaffins.

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Received November 14, 1956

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*Original Russian pagination. See C. B. Translation.

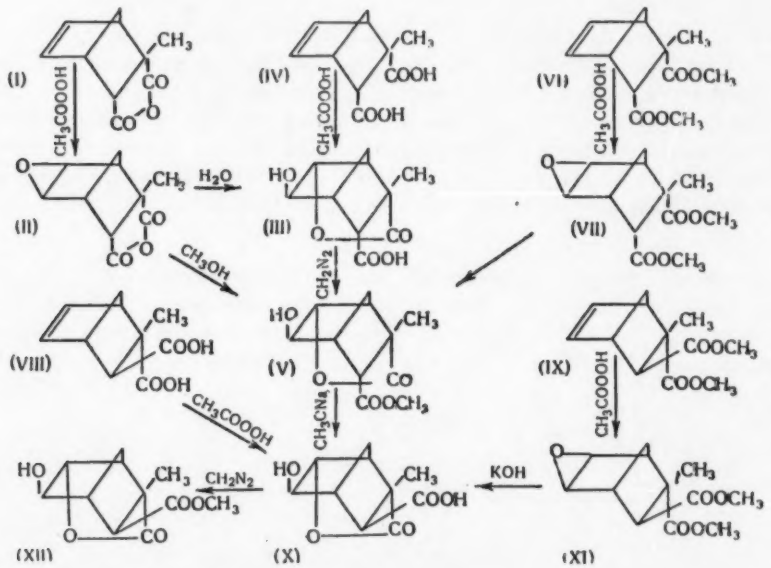
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 21. EPOXIDES OF ISOMERIC 2-METHYLBICYCLO[2.2.1]HEPT-5-ENE-2,3-DICARBOXYLIC ACIDS AND THEIR REACTIONS

I. N. Nazarov, V. F. Kucherov, and V. G. Bukharov

As shown in the preceding communication [1], oxidation of the isomeric dicarboxylic acids of the bicyclo-[2.2.1]hept-2-ene series with peroxyacetic acid leads to the corresponding epoxides having an exo configuration of the epoxy ring, and these can be lactonized readily only when the carboxy groups are in the endo position. In the further study of the course and stereochemistry of these reactions, we have examined the transformations of the epoxides for the case of the isomeric 2-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acids and their derivatives, which were obtained previously in the condensation of cyclopentadiene with citraconic anhydride [2].

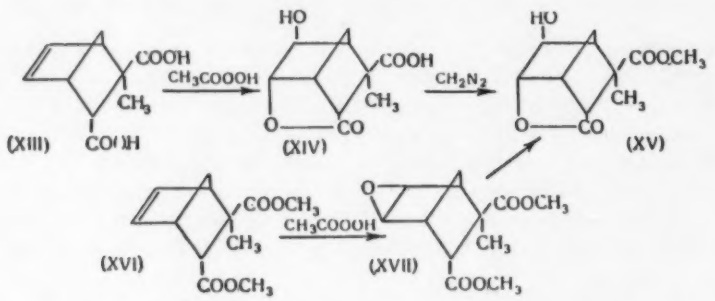
Oxidation of the endo anhydride (I) with peroxyacetic acid in chloroform gave only one epoxide, the oxo epoxide (II), in good yield; this product was readily hydrolyzed by water to the hydroxy γ-lactone acid (III). Ready lactonization with formation of the hydroxy γ-lactone acid (III) occurred also in the direct oxidation of the endo acid (IV) and, as already noted [1], resulted from endo addition of carboxyl at the endo-epoxy ring formed. In the same way, boiling of the epoxy endo anhydride (II) with absolute methanol resulted in quantitative formation of the hydroxy γ-lactone ester (V), which was obtained also by treatment of the hydroxy γ-lactone acid (III) with diazomethane. Oxidation of the endo diester (VI) also results in the formation of only one epoxide, the exo epoxide (VII), which gives the above-described hydroxy γ-lactone ester (V) on acid hydrolysis.



The exo position of the hydroxy group in the presence of a γ-lactone ring in the hydroxy γ-lactone acid (III)

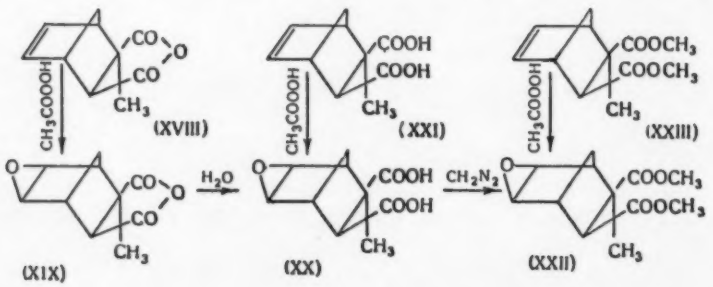
was readily proved by the fact that the substance was found to be incapable of lactonization despite the endo configuration of the free carboxy group and gave only the corresponding acetic ester when treated with acetyl chloride (the infrared spectrum of the acetic ester contained a carbonyl absorption band at 5.6 μ characteristic for the γ--lactone grouping [3].

Final proof of the structure of the hydroxy γ-lactone acid (III) was obtained by the oxidation of the trans acid (VIII) and its ester (IX), which contain a tertiary endo carboxy group. When treated with peroxyacetic acid, the trans acid (VIII) gave a good yield of the hydroxy γ-lactone acid (X), which was obtained also by the alkaline hydrolysis of the epoxy trans diester (XI). Treatment of the hydroxy γ-lactone acid (X) with diazomethane gave the corresponding hydroxy γ-lactone ester (XII), the acetic ester of which gave the γ-lactone absorption band at 5.6 μ. In accordance with the configuration of the trans acid (VIII), lactonization of the corresponding epoxide can proceed only at the tertiary endo carboxy group, as a result of which the hydroxy γ-lactone acid (X) formed would have a free secondary exo carboxy group. If lactonization of the epoxy endo anhydride (II) proceeds with participation of the tertiary carboxy group, then the hydroxy γ-lactone acid (III) should be the epimer of the hydroxy γ-lactone acid (X) at the secondary carboxy group. We succeeded in confirming this experimentally, for it was found that, on isomerization with sodium methoxide, the hydroxy γ-lactone ester (V) gave a good yield of the hydroxy γ-lactone acid (X). This constitutes strict proof that the hydroxy γ-lactone acid (III) has a free secondary endo carboxy group, so that lactonization of the epoxy endo anhydride (II) proceeds at the tertiary carboxyl, as in the case of the direct lactonization of the endo acid (IV) with 50% sulfuric acid [2]. In the hydroxy lactone acid system the exo position of the carboxy and hydroxy groups is found to be the more stable, as already noted in the case of the oxidation of isomeric bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acids [1].



The isomeric trans acid (XIII) with an endo secondary carboxy group was also found to be capable of lactonization during oxidation with peroxyacetic acid, when it gave the hydroxy γ-lactone acid (XIV), which was converted into the crystalline hydroxy γ-lactone ester (XV) by the action of diazomethane. The structure of the ester was readily proved by the fact that it was incapable of being isomerized by sodium methoxide, did not form a lactone under lactonization conditions, and gave an acetic ester having a carboxyl absorption band characteristic of the γ-lactone ring (6.50 μ). Oxidation of the trans diester (XVI) with peroxyacetic acid gave the stable epoxide (XVII), which formed a lactone only when submitted to acid hydrolysis, when the hydroxy γ-lactone ester (XV) was was formed.

As would be expected, owing to the exo configuration of the carboxy groups, oxidation of the exo anhydride (XVIII) is not accompanied by lactonization and leads to the stable epoxide (XIX), which is hydrolyzed by water to the epoxy exo acid (XX). This acid is obtained by oxidation of the exo acid (XXI) and with diazomethane gives the epoxy exo diester (XXII), which is formed in almost quantitative yield also by the oxidation of the exo diester (XXIII).



The exo configuration of the epoxy ring in all the epoxides described was confirmed, as in the previous case [1], by hydrogenation under pressure in presence of a nickel catalyst. Because of the nonsymmetry of the molecule the product was a mixture of isomeric hydroxy acids, which we did not succeed in resolving. However, the fact that these hydroxy acids did not give lactones and all of the above-described lactonizations at the epoxy ring were completely analogous with the corresponding transformations described for the isomeric bicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic acids [1] gave us grounds for the view that in this case also the epoxy ring had the exo configuration.

EXPERIMENTAL

Epoxy Endo Anhydride (II)

A solution of the endo anhydride (I) [4] in 10 ml of dry chloroform was taken, and 1.8 ml (100% excess) of 95% peroxyacetic acid was added; the mixture was left at room temperature for two days. Solvent and excess of peroxyacetic acid were vacuum-distilled off, and crystallization of the residue from 1 : 1 benzene-ether gave 1 g of the epoxide (II), m.p. 219-220°.

Found %: C 61.54; H 5.27. $C_{10}H_{10}O_4$. Calculated %: C 61.85; H 5.20.

Epoxy Endo Diester (VII)

With cooling, 7.5 ml of 50% peroxyacetic acid was added slowly to a solution of 10 g of the endo diester (VI) [2] in 50 ml of dry chloroform, and the mixture was left at 0° overnight. The solution was washed with cold water and sodium bicarbonate solution, and was dried with sodium sulfate; sovent was vacuum-distilled off. The liquid residue gradually solidified and gave 10 g of the epoxide (VII), m.p. 66-68°, raised to 68-69° by crystallization from petroleum ether.

Found %: C 59.97; 60.01; H 6.72; 6.67. $C_{12}H_{16}O_5$. Calculated %: C 59.99; H 6.71.

Hydroxy Lactone Acid (III)

a) To a stirred solution of 3.5 g of the endo cis acid (IV) [5] in 10 ml of glacial acetic acid, 3 ml of 90% peroxyacetic acid was added slowly. The mixture was left overnight, and the precipitate formed was filtered off and washed with ether. Crystallization from water gave 2.2 g of pure hydroxy γ-lactone acid (III), m.p. 192-193°; found M: 213.7 (by titration); calculated M: 212.2.

Found %: C 56.41; 56.55; H 5.80; 5.71. $C_{10}H_{12}O_5$. Calculated %: C 56.60.

b) A mixtureof 0.7 g of the endo anhydride (II) and 2 ml of water was boiled until solution was complete. When the solution cooled, crystals appeared and were recrystallized from a little water. The product, amounting to 0.45 g, was the hydroxy γ-lactone acid (III), m.p. 192-193°, identical with that of the product described above.

Hydroxy γ-Lactone Ester (V)

a) A suspension of 0.5 g of the hydroxy γ-lactone acid (III) in ether was treated with ethereal diazomethane; ether was distilled off, and recrystallization from a 2 : 1 mixture of ether and petroleum ether gave 0.4 g of the hydroxy γ-lactone ester (V), which melted constantly at 63-64°.

Found %: C 58.42; 58.28; H 6.25; 6.38. $C_{11}H_{14}O_5$. Calculated %: C 58.40; H 6.23.

When crystallized from water, the hydroxy γ-lactone ester (V) gave a crystal hydrate of m.p. 72-73°, which lost water when vacuum-dried with quantitative formation of the anhydrous product, m.p. 63-64°. Boiling of the hydroxy γ-lactone ester (V) with excess of acetyl chloride gave a good yield of the corresponding acetic ester, which melted at 106-107° after crystallization from 1 : 2 benzene-ether.

Found %: C 58.19; 57.45; H 5.92; 5.81. $C_{13}H_{16}O_6$. Calculated %: C 58.20; H 6.01.

b) A solution of 0.5 g of the epoxy endo anhydride (II) in 30 ml of absolute methanol was boiled for one hour; methanol was distilled off, and the crystalline residue was washed on the filter with a 1 : 1 mixture of diethyl ether and petroleum ether. The product, amounting to 0.5 g, was the hydroxy γ-lactone ester (V), m.p. 62-63°, undepressed by admixture of the above-described sample.

c) A solution of 0.5 g of the epoxy endo diester (VII) in 5 ml of 90% peroxyacetic acid was left at room temperature for six days, after which it was evaporated in a vacuum. The liquid residue crystallized when treated with a little water and yielded 0.45 g of the crystal hydrate of the hydroxy γ-lactone ester (V), m.p. 72-73°, undepressed by admixture of the above-described sample.

Epoxy Trans Diester (XI)

To a solution of 1.6 g of the trans diester (IX) in 8 ml of dry chloroform, 1.2 ml of 90% peroxyacetic acid was added, and the mixture was left overnight at 0°. The solution was washed with cold water and sodium bicarbonate solution, and chloroform was vacuum-distilled off. The crystalline oxidation product was washed with petroleum ether. The yield of the epoxide (XI), m.p. 73-75°, was 1.6 g; after recrystallization from petroleum ether it it melted at 76-77°.

Found %: C 60.11; 60.03; H 6.92; 6.83. $C_{12}H_{16}O_5$. Calculated %: C 59.99; H 6.71.

Hydroxy γ-Lactone Acid (X)

a) A solution of 1 g of the trans acid (VIII) [5] in 5 ml of glacial acetic acid was prepared, 0.9 ml of 90% peroxyacetic acid was added, and the mixture was left at room temperature for ten days. The precipitate formed was filtered off and washed with ether. The yield of the hydroxy γ-lactone acid (X), m.p. 201-203°, was 0.7 g; after recrystallization from water it melted at 203-204°; found M: 213.7 (by titration); calculated M: 212.2.

Found %: C 56.44; 56.46; H 5.60; 5.55. $C_{10}H_{12}O_5$. Calculated %: C 56.60; H 5.70.

b) The hydroxy γ-lactone ester (V) (1.2 g) was added to a solution of 3 g of sodium in 60 ml of absolute methanol, and the mixture was boiled for 16 hours. Methanol was distilled off, water was added to dissolve the residue, and the mixture was boiled for two hours, filtered with addition of charcoal, and acidified. The product, amounting to 0.8 g, was the hydroxy γ-lactone acid (X), m.p. 203-204°, identical with that of the sample described above.

c) A mixture of 1.5 g of the epoxy trans ester (XI) and 20 ml of a 15% aqueous-methanolic (1 : 1) solution of potassium hydroxide was boiled for 15 hours; methanol was distilled off. Acidification with hydrochloric acid gave 0.8 g of the hydroxy γ-lactone acid (X), which melted at 203-204° after crystallization from water and showed no depression of melting point in admixture with the samples described above.

Hydroxy γ-Lactone Ester (XII)

A suspension of 0.5 g of the hydroxy γ-lactone acid (X) in ether was treated with ethereal diazomethane; ether was distilled off, and crystallization from ether gave 0.4 g of the hydroxy γ-lactone ester (XII), which melted constantly at 107-108°.

Found %: C 58.55; 58.44; H 6.17; 6.14. $C_{11}H_{14}O_5$. Calculated %: C 58.40; H 6.23.

Boiling of the hydroxy γ-lactone ester (XII) with acetyl chloride resulted in a good yield of the corresponding acetic ester, which melted at 113-114° after crystallization from a 1 : 2 mixture of benzene and petroleum ether.

Found %: C 58.45; 58.46; H 5.92; 6.05. $C_{13}H_{16}O_6$. Calculated %: C 58.20; H 6.01.

Epoxy Trans Diester (XVII)

With cooling, 1.2 ml of 95% peroxyacetic acid was added to a solution of 1.5 g of the trans diester (XVI) [2] in 8 ml of dry chloroform, and the mixture was left overnight at 0°. Solvent was vacuum-distilled off, and crystallization of the residue from petroleum ether gave 1.4 g of the pure epoxide (XVII), m.p. 64-65°.

Found %: C 59.70; 59.59; H 6.75; 6.57. $C_{12}H_{16}O_5$. Calculated %: C 59.99; H 6.71.

Hydroxy γ-Lactone Acid (XIV)

Slowly, with stirring, 1.6 ml of 90% peroxyacetic acid was added to a solution of 2 g of the trans acid (XIII) [2] in 10 ml of glacial acetic acid; the mixture was left for ten days at room temperature, after which acetic acid was vacuum-distilled off. The residue was treated with ether, and the crystalline product was filtered off.

The product, amounting to 1.7 g, was the hydroxy γ-lactone acid (XIV), m.p. 185-186° crystallization from ethyl acetate did not affect the melting point; found M: 207.0 (by titration); calculated M: 212.2.

Found %: C 56.57; 56.87; H 5.79; 5.71. $C_{10}H_{12}O_5$. Calculated %: C 56.60; H 5.70.

Hydroxy γ-Lactone Ester (XV)

a) A suspension of 1.2 g of the hydroxy γ-lactone acid (XIV) in ether was treated with ethereal diazomethane, ether was distilled off, and crystallization from benzene gave 1.1 g of the hydroxy γ-lactone ester (XV), m.p. 130-131°.

Found %: C 58.33; 58.32; H 6.24; 6.33. $C_{11}H_{14}O_5$. Calculated %: C 58.40; H 6.23.

Boiling of the hydroxy γ-lactone ester (XV) with acetyl chloride gave a quantitative yield of the corresponding acetic ester, which melted at 127-128° after crystallization from 1 : 1 benzene-ether and showed depression of melting point in admixture with the original hydroxy γ-lactone ester (XV).

Found %: C 58.24; 58.04; H 6.01; 6.00. $C_{13}H_{16}O_6$. Calculated %: C 58.20; H 6.01.

b) A solution of 0.5 g of the epoxy trans diester (XVII) in 5 ml of 90% acetic acid was heated at 50° for two hours, acetic acid was vacuum-distilled off, and the residue was treated with a little water. The crystalline product was filtered off; crystallization from benzene gave 0.25 g of the hydroxy γ-lactone ester (XV), m.p. 129-130°, identical with the products described above.

Epoxy Exo Anhydride (XIX)

To a solution of 2.2 g of the exo cis anhydride (XVIII) in 10 ml of dry chloroform, 2 ml of 95% peroxyacetic acid was added gradually; the mixture was left overnight at room temperature. The solution was evaporated in a vacuum, the residue was treated with ether, and the crystalline oxidation product was filtered off. The yield of the epoxide (XIX) was 1.4 g; after one crystallization from benzene it had a constant melting point of 228-229°.

Found %: C 61.94; 61.93; H 5.19; 5.23. $C_{10}H_{10}O_4$. Calculated %: C 61.85; H 5.20.

Epoxy Exo Acid (XX)

a) To a solution of 0.5 g of the exo cis acid (XXI) [2] in 2 ml of glacial acetic acid, 0.4 ml of 90% peroxyacetic acid was added and the mixture was left at room temperature for two days. The crystalline product was filtered off and washed with ether. Crystallization from water gave 0.3 g of the epoxide (XX), m.p. 226-227° (with decomposition).

Found %: C 56.46; 56.47; H 5.66; 5.82. $C_{10}H_{12}O_5$. Calculated %: C 56.60; H 5.70.

b) The epoxy exo anhydride (XIX) (0.7 g) was boiled with 2 ml of water until dissolved; cooling yielded 0.6 g of the epoxy exo acid (XX), m.p. 225-226°, undepressed by admisture of the sample described above. According to titration with alkali, this epoxy exo acid contains two free carboxy groups.

Epoxy Exo Diester (XXII)

To a solution of 2 g of the exo-cis diester (XXIII) in 10 ml of dry chloroform, 1.4 ml of 95% peroxyacetic acid was added with cooling; the mixture was left overnight. The solution was washed with water and sodium bicarbonate solution; it was dried with sodium sulfate, and chloroform was distilled off. The liquid residue gradually solidified. The product, amounting to 1.9 g, was the epoxide (XXII), which melted at 60-61° after crystallization from ether.

Found %: C 60.01; 59.93; H 6.68; 6.69. $C_{12}H_{16}O_5$. Calculated %: C 59.99; H 6.71.

Treatment of the epoxy exo acid (XX) with ethereal diazomethane gave a quantitative yield of the above-described epoxy exo diester (XXII), m.p. 59-60°

SUMMARY

1. An investigation was made of the oxidation of the isomeric 2-methylbicyclo[2.2.1]hept-5-ene-2,3-di-

carboxylic acids and their derivatives with peroxyacetic acid, and the reactions of the epoxides formed were studied.

2. The structures of the isomeric hydroxy γ-lactone acids (III) and (X) were proved, and it was shown that intramolecular lactonization at the epoxy ring proceeds preferentially with the tertiary carboxy group.

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Received September 7, 1956

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ACETYLENE DERIVATIVES

COMMUNICATION 180. AMINES OF THE 1-BUTEN-3-YNE SERIES. EFFECT OF TRACES OF IRON ON THE MANNICH REACTION WITH 1-BUTEN-3-YNE HYDROCARBONS

I. N. Nazarov and E. A. Mistriukov

Amines of the 1-buten-3-yne series were first prepared by Coffman in 1935 [1] by heating 1-buten-3-yne, paraform, and a dialkylamine in dioxane solution:

$$CH_2=CH-C\equiv CH \xrightarrow[\text{dioxane}]{CH_2O,\ R_2NH} CH_2=CH-C\equiv C-CH_2-NR_2.$$

When attempts were made to extend the Mannich reaction to 1-buten-3-yne homologs, no reproducible results were obtained until it was realized that the success of this synthesis was dependent on the presence of extraneous iron compounds in the paraform. Different samples of paraform gave widely differing results, and yields of aminomethylation products from 1-buten-3-yne hydrocarbons varied under given conditions from 15-20% to 90%, depending on the quality of the paraform used. Carefully purified paraform and diethylamine scarcely reacted at all with 1-buten-3-yne hydrocarbons, even when heated for a long time. Only when catalytic amounts of iron salts ($FeCl_3$) were added to the reaction mixture did the formation of aminomethyl derivatives proceed smoothly in yields of about 90%:

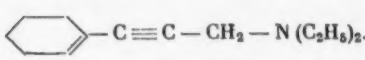
$$-CH=\overset{|}{C}-C\equiv CH \xrightarrow[Fe^{3+},\ \text{dioxane}]{CH_2O,\ H\,N(C_2H_5)_2} -CH=\overset{|}{C}-C\equiv C-CH_2-N(C_2H_5)_2$$

This reaction was slightly accelerated also by the addition of hydrochloric acid.

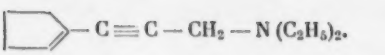
Aminomethylation was effected by heating diethylamine, paraform, and the 1-buten-3-yne hydrocarbon in dioxane solution in presence of small amounts of ferric chloride. In this way we aminomethylated 2-methyl-1--buten-3-yne, 3-methyl-3-penten-1-yne, 1-ethynylcyclohexene, 1-ethynylcyclopentene, and 3-penyl-3-penten--1-yne and obtained the following amines of the 1-buten-3-yne series: N,N-diethyl-4-methyl-4-penten-2-ynylamine (I), N,N-diethyl-4-methyl-4-hexen-2-ynylamine (II), 3-(1-cyclohexen-1-yl)-N,N-diethyl-2-propynylamine (III), 3-(1-cyclopenten-1-yl)-N,N-diethyl-2-propynylamine (IV), and N,N-diethyl-4-phenyl-4-hexen-2-ynylamine (V):

$$CH_2=\overset{CH_3}{\overset{|}{C}}-C\equiv C-CH_2-N(C_2H_5)_2. \quad (I)$$

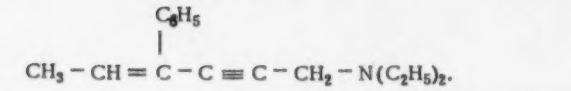
$$CH_3-CH=\overset{CH_3}{\overset{|}{C}}-C\equiv C-CH_2-N(C_2H_5)_2. \quad (II)$$



$$-C\equiv C-CH_2-N(C_2H_5)_2. \quad (III)$$



(IV)



(V)

The 1-buten-3-yne hydrocarbons used in the Mannich reaction were prepared by the dehydration of acetylenic alcohols by means of phosphoryl chloride in pyridine or by pyrolysis of the acetic esters. 3-Phenyl-3-penten-1-yne is extremely unstable, and it was therefore aminomethylated in the unpurified state.

The pentenynylamine (I)-(V) are stable liquids which do not change appreciably when distilled or kept without access of air. Their picrates decompose rapidly when kept in the light. Their hydrochlorides are still less stable. The structure of these amines follows from the method of preparation, their reactions (see future communications), and the agreement of the constants of amines (III) and (IV) with those of the same compounds prepared in another way [2].

EXPERIMENTAL

2-Methyl-1-buten-3-yne [3]. This was prepared by an improved modification of Thompson's method. A mixture of 800 ml of acetic anhydride and 30 g of p-toluenesulfonic acid was prepared in a round-bottomed flask, and 504 g of 2-methyl-3-butyn-2-ol was added with cooling. When the exothermic reaction was complete, 5 g of finely ground pumice was added; the flask was provided with a 40-cm fractionation column and was heated cautiously until the vigorous liberation of hydrocarbon began. Heating was controlled so that the temperature of the vapor did not rise above 90°. Reaction was complete in 1-1.5 hours. Redistillation of the distillate gave 250 g (63%) of 2-methyl-1-buten-3-yne, b.p. 35-38°.

3-Methyl-3-penten-1-yne. An acetic ester was prepared, as in the previous experiment, from 3-methyl--1-pentyn-3-ol (300 g) and acetic anhydride (340 ml) in presence of p-toluenesulfonic acid (15 g). The acetic ester was distilled in presence of 3 g of ground pumice through a 40-cm fractionating column. In the course of 90 minutes the temperature of the vapor rose gradually to 120° and then kept at about 121° for a further 30 minutes. The distillate was diluted with an equal volume of water, and the hydrocarbon layer was washed with sodium hydroxide solution, dried with potassium carbonate, and distilled. A fraction of b.p. 66-69° was collected; yield 125.2 g (52%) [4].

1-Ethynylcyclohexene. This was prepared by the dehydration of 1-ethynylcyclohexanol with phosphoryl chloride and pyridine [5].

1-Ethynylcyclopentene. A solution of 110 ml of phosphoryl chloride in 110 ml of pyridine was added gradually to a solution of 180 g of 1-ethynylcyclopentanol in 300 ml of pyridine at 90-100° (cooling). The reaction mixture was heated at 90° for 40 minutes and then poured rapidly onto ice; the hydrocarbon was extracted with ether, and the ether extract was washed with dilute hydrochloric acid and with water. The extract was dried, and distillation then gave 117.3 g (78%) of 1-ethynylcylopentene, b.p. 59-61° (110 mm); $n^{18}D$ 1.4890 [6].

3-Phenyl-3-penten-1-yne. A solution of 58 ml of phosphoryl chloride in 58 ml of pyridine was added over a period of 30 minutes to a solution of 140 g of 3-phenyl-1-pentyn-3-ol in 160 ml of pyridine at 70-75° (cooling with water). The reaction mixture was then heated at 70° for 30 minutes and poured onto ice; the product was extracted with ether, and the extract was washed with water, dried with potassium carbonate, and vacuum-distilled. A fraction (78.2 g) of b.p. 69-71° (0.5 mm) and $n^{20}D$ 1.5620 was collected; it consisted essentialy of 3-phenyl--3-penten-1-yne. This hydrocarbon was aminomethylated without further purification.

N,N-Diethyl-4-methyl-4-penten-2-ynylamine (I). Diethylamine (234 ml, i.e., 2.28 moles) as added (rapidly !) to 75 g (2.5 moles) of paraform contained in a flask fitted with reflux condenser. When the exothermic reaction stopped, the resulting solution of the hydroxymethyl derivative was cooled and transferred to a one-liter stainless steel reactor fitted with stirrer; to this was added 212 ml (2.27 moles) of 2-methyl-1-buten-3-yne and 300 ml of dioxane to which a few crystals of ferric chloride had been added. The reactor was filled with nitrogen at 30-40 atm, and was then heated at 95-100° for 15 hours. The cooled reaction mixture was neutralized with dilute sulfuric acid (65 ml of concentrated acid and 200 ml of water), dioxane and part of the water was removed under reduced pressure, and the base was liberated by means of concentrated sodium hydroxide or ammonia solution;

it was washed with water (150 ml), dried with potassium carbonate, and vacuum-distilled. The yield of N,N--diethyl-4-methyl-4-penten-2-ynylamine, b.p. 61-62° (7 mm), was 284 g (83%); $n^{21}D$ 1.4658.

Found %: N 9.17; $C_{10}H_{17}N$. Calculated %: N 9.27.

The picrate had m.p. 93-93.5° (from alcohol). The hydrochloride, prepared by passing dry hydrogen chloride into an ethereal solution of the amine, had m.p. 125-126° (from butanone) and decomposed rapidly when kept.

Aminomethylation of Higher 1-Buten-3-yne Homologs

N,N-Diethyl-4-methyl-4-hexen-2-ynylamine (II). A hydroxymethyl derivative was prepared from 270 ml (2.62 moles) of diethylamine and 76.2 g (2.54 moles) of paraform in a round-bottomed flask fitted with reflux condenser, as indicated above, and to the resulting solution 184 g (2.3 moles) of 3-methyl-3-penten-1-yne and 250 ml of dioxane containing a little ferric chloride were added. The reaction mixture was boiled for 15-18 hours, during which time the temperature rose gradually from 80° to 105°; the mixture was then neutralized with 540 ml of 5 N HCl with cooling. Dioxane and part of the water were removed below 50° under reduced pressure; the base was liberated by addition of concentrated ammonia solution and extracted with ether. The solution was dried with potassium carbonate, and vacuum distillation then gave 339.5 g (89%) of N,N-diethyl-4-methyl-4-hexen-2--ynylamine; b.p. 86-89° (12-13 mm); $n^{19.5}D$ 1.4735.

Found %: N 8.40. $C_{11}H_{19}N$. Calculated %: N 8.48.

The picrate had m.p. 98-99° (from alcohol), and the hydrochloride, prepared as in the preceding case, had m.p. 126-127° (from dioxane).

3-(1-Cyclohexen-1-yl)-N,N-diethyl-2-propynylamine (III). Under the conditions of the previous experiment 23.5 g of paraform, 80 ml of diethylamine, and 75 g of 1-ethynylcyclohexene [5] reacting in 120 ml of dioxane gave 122.1 g (91%) of 3-(1-cyclohexen-1-yl)-N,N-diethyl-2-propynylamine; b.p. 104-106° (1-1.5 mm); $n^{21}D$ 1.5008. The literature [2] gives b.p. 78° (0.2 mm); $n^{18}D$ 1.5001.

Found %: N 7.54. $C_{13}H_{21}N$. Calculated %: N 7.35.

The picrate had m.p. 104-105° (from alcohol).

3-(1-Cyclopenten-1-yl)-N,N-diethyl-2-propynylamine (IV). Under the conditions indicated above 21.6 g of paraform, 74 ml of diethylamine, and 60 g of 1-ethynylcyclopentene [6] reacting in 110 ml of dioxane gave 94.7 g (82%) of 3-(1-cyclopenten-1-yl)-N,N-diethyl-2-propynylamine; b.p. 57° (0.2 mm); $n^{16}D$ 1.4995.

Found %: N 7.88. $C_{12}H_{19}N$. Calculated %: N 7.92.

The picrate had m.p. 77-78° (from alcohol).

N,N-Diethyl-4-phenyl-4-hexen-2-ynylamine (V). A mixture of 4.8 g of paraform, 16.5 ml of diethylamine, and 20.4 g of unpurified 3-phenyl-3-penten-1-yne in 30 ml of dioxane was heated in a steam bath for 22 hours, and and the usual treatment then gave 23.12 g (71%) of N,N-diethyl-4-phenyl-4-hexen-2-ynylamine; b.p. 115-122° (0.5 mm); $n^{20}D$ 1.5450.

Found %: C 84.44; H 9.24; N 6.26. $C_{16}H_{21}H$. Calculated %: C 84.5; H 9.25; N 6.17.

The picrate had m.p. 114.5-115.5° (from alcohol).

Effect of Catalytic Amounts of Ferric Chloride on the Aminomethylation of 3-Methyl-3-penten-1-yne

In a flask fitted with reflux condenser and a wide electrically heated tube for the passage of gas, 150 ml (1.46 moles) of diethylamine was heated to the boil (water bath) with simultaneous passage of formaldehyde vapor obtained by the depolymerization of 52 g of paraform. Dioxane (200 ml) and 3-methyl-3-penten-1-yne (105 g) were added to the solution formed, after which the mixture was divided into three equal parts: 1) to the first part 5 ml of dioxane containing about 0.2 g of dissolved ferric chloride hydrate was added; 2) to the second part 5 ml of dioxane containing 0.5 ml of concentrated hydrochloric acid was added; 3) to the third part 5 ml of dioxane was added.

All three parts were refluxed in a water bath at 90-97° for 20 hours and were then treated identically: a

solution of 50 ml of concentrated hydrochloric acid in 150 ml of water was added, unchanged hydrocarbon was extracted with 40 ml of dibutyl phthalate, the aqueous solution was vacuum-evaporated down to about 100 ml, and the base was liberated by addition of 80 ml of concentrated ammonia solution and extracted with 40 ml of ether. In the distillation of the base and unchanged hydrocarbon we obtained:

1) in the first case (with ferric chloride) 3.5 g of unchanged hydrocarbon (b.p. 66-70°) and 56.8 g of the hexenynylamine (II), b.p. 86-89° (12 mm); yield 79%;

2) in the second case (with concentrated hydrochloric acid) 28 g of unchanged hydrocarbon (b.p. 66-70°) and 10.0 g of the hexenynylamine (II), b.p. 86-89° (12 mm); yield 13.8%;

3) in the third case (no catalyst) 33 g of unchanged hydrocarbon (b.p. 66-70°) and 2.2 g of the amine (II), b.p. 86-89° (12 mm); yield 3.5%.

SUMMARY

1. It was shown that the presence of catalytic amounts of iron salts has a powerful effect on the course of the aminomethylation of 1-buten-3-yne hydrocarbons.

2. Several 1-buten-3-yne hydrocarbons were aminomethylated in high yield.

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Received November 19, 1956

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SYNTHESIS AND REACTIONS OF DIVINYL ETHER

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It is reported in the literature that divinyl ether is a fairly powerful anesthetic; under the name of Vinethene it is recommended for use in surgical practice for minor operations. Nothing is known concerning the applicability of divinyl ether in other fields. The present investigation was undertaken with the object of learning more of the chemical properties of divinyl ether and of some of its halogen derivatives.

Divinyl ether $CH_2=CHOCH=CH_2$ was prepared by Semmler [1] in 1887 by an exchange reaction between natural divinyl sulfide and dry silver oxide. Later methods of preparing divinyl ether were based on the investigations of Knorr and Matthes [2], Cretcher, Koch, and Pittenger [3], Hibbert, Perry, and Taylor [4], Ruigh and Major [5], and other authors [6-10]. We prepared divinyl ether in 65% yield by adding bis-2-chloroethyl ether slowly to a solution of potassium hydroxide in triethanolamine heated to 160° with containuous removal of the product from the sphere of reaction.

Divinyl ether is a clear colorless volatile mobile liquid having an ethereal odor; it is insoluble in water. As an unsaturated compound it decolorizes bromine instantly, is oxidized by permanganate solution, and reacts vigorously with concentrated sulfuric acid with formation of a black resin. When treated with hydrochloric acid it turns yellow and forms acetaldehyde [5]. Heating, particularly in presence of benzoyl peroxide, converts it into a polymer [4]. Ammonia retards this reaction.

The polymerization of divinyl ether is not induced by ferric or stannous chloride. By its ability to polymerize by a free-radical mechanism, divinyl ether is very sharply distinguished from alkyl vinyl ether, which polymerize by the ionic mechanism. Divinyl ether polymer prepared in the presence of benzoyl peroxide is a solid substance that is insoluble in water and in the usual organic solvents. Pure divinyl ether is a rather unstable compound. When kept for a short time, even in a sealed tube, it changes spontaneously into a solid substance, evidently under the action of atmospheric oxygen; in order to stabilize it ammonia [11] or amines, such as N-phenylnaphthylamine [12], are added.

In a study of the properties of divinyl ether we investigated its behavior toward 2% sulfuric acid solution, hydrogen chloride, chlorine, and bromine. A kinetic investigation of its hydrolysis [13] with weak aqueous solutions of hydrochloric acid or with benzenesulfonic acids at 25° showed that divinyl ether is split quantitatively as follows:

$$CH_2=CHOCH=CH_2 + H_2O \xrightarrow{HCl} 2CH_3C\begin{matrix}=O\\ \diagdown H\end{matrix}$$

the only product being acetaldehyde. It was shown also that the reaction proceeds considerably more readily than in the case of alkyl vinyl ethers. We carried out the hydrolysis of divinyl ether by heating it with 2% sulfuric acid. The extent of hydrolysis was determined from the acetaldehyde content of the products, which was determined by the bisulfite method. Under these conditions divinyl ether is hydrolyzed almost completely in accordance with the above scheme.

The addition of hydrogen chloride was carried out by the method developed for the hydrohalogenation of alkyl vinyl ethers [14]: hydrogen chloride was passed slowly into cooled divinyl ether. The reaction proceeded stagewise, as follows:

1. $CH_2=CHOCH=CH_2 + HCl \rightarrow CH_2=CHOCHClCH_3$

2. $CH_2=CHOCHClCH_3 + HCl \rightarrow HCl = CH_3CHClOCHClCH_3$

The addition of one molecule of hydrogen chloride gave 1-chloroethyl vinyl ether, and the addition of two molecules gave bis-1-chloroethyl ether. In comparison with alkyl 1-chloroethyl ethers, these chloro ethers were fairly stable when kept in sealed tubes. The high mobilities of the 1-chlorine and 2-hydrogen atoms, which were similar to those in alkyl 1-chloroethyl ethers, made it possible to apply the method of analysis developed for alkyl 1-chloroethyl ethers [14].

The chlorination was carried out by the method developed for the synthesis of alkyl 1,2-dichloroethyl ethers [15]: passage of chlorine into cooled divinyl ether to complete saturation. An attempt to bring about stagewise chlorination with the object of isolating the intermediate 1,2-dichloroethyl vinyl ether,

$$CH_2 = CHOCH = CH_2 + Cl_2 \rightarrow CH_2 = CHOCHClCH_2Cl$$

led to the formation of a difficultly separable mixture of chlorine-containing compounds.

Bis-1,2-dibromoethyl ether $CH_2BrCHBrOCHBrCH_2Br$ has been prepared by the addition of bromine to divinyl ether in chloroform [4] or in diethyl ether [6]. We synthesized this compound by slow addition of bromine to a cooled solution of divinyl ether in carbon tetrachloride. Bis-1,2-dibromoethyl ether forms clear colorless needles, stable to storage. The recrystallized ether melted sharply. The occurrence of diastereoisomerism, referred to by some authors [16], was not detected.

EXPERIMENTAL

Preparation of Divinyl Ether. The reaction was carried out in a 250-ml round bottomed flask fitted with mechanical stirrer with a glycerol seal, reflux condenser, thermometer, and dropping funnel. The condenser was connected to a coil receiver immersed in a cooling mixture (−25°). With the object of removing divinyl ether from the sphere of reaction as fast as it was formed, warm water (35°) was passed through the condenser. A mixture of 15 g of triethanolamine and 100 g of potassium hydroxide powder was prepared in the flask and was heated with stirring to 160°. At this temperature 40 g of bis-2-chloroethyl ether (b.p. 91° (37 mm); d^{20}_4 1.2182; $n^{20}D$ 1.4570) was added slowly from a dropping funnel to the alkaline solution. Reaction continued for seven hours. The product that collected in the receiver was washed three times with cold water and dried with calcium chloride; it was then left over sodium and finally distilled over sodium. The product, amounting to 15 g (65%), was pure divinyl ether, b.p. 28.3-28.5° (752 mm); d^{20}_4 0.7734; $n^{20}D$ 1.3982. The literature gives: b.p. 39° [1, 3]; 34-35° [4]; 28.3 ± 0.2° (760 mm) [5]; 28-28.5° [6]; 28-29° [7, b]; 28.35° ± 0.04 [10]; 28.49° (765 mm) [11]; f.p. −101.1° [11]; d^{20}_4 0.774; d^{20}_4 0.773 [5]; d^{20}_4 0.7729 [6]; $n^{20}D$ 1.3989 [5, 11].

Hydrolysis of Divnyl Ether. A mixture of 0.2755 g of the ether and 25 ml of 2% sulfuric acid solution was heated in a sealed tube for two hours at 80°. The reaction mixture was transferred quantitatively to a measuring flask and diluted with distilled water to 250 ml. The amount of acetaldehyde formed was determined by the bisulfite method: 25 ml of 0.1 N sodium bisulfite and 16.51 ml of the solution under test were introduced into an Erlenmeyer flask having a ground-in stopper; the mixture was shaken and placed on ice, and after 30 minutes unchanged bisulfite was titrated with 0.1 N iodine. A control experiment was carried out to determine the titer of the bisulfite. The amount of acetaldehyde bound by the bisulfite corresponded to 9.8 ml of 0.1 N iodine. This shows that the ether was hydrolyzed to the extent of 94.4%.

Synthesis of 1-Chloroethyl Vinyl Ether. Pure divinyl ether (10 g) was placed in a flask fitted with glycerol-sealed mechanical stirrer, thermometer, and tube, reaching to the bottom, for the passage of gas. The reaction flask was immersed in a cooling mixture (−10°), and a slow stream of dry hydrogen chloride was passed with vigorous stirring of the ether. Reaction proceeded for about one hour at not above 10°. Reaction was terminated when the theoretical increase of weight had occurred. Vacuum distillation of the reaction product gave 10 g (60%) of pure 1-chloroethyl vinyl ether, a colorless mobile liquid. It fumes in the air and decolorizes bromine; b.p. 25° (31 mm); d^{20}_4 1.0232; $n^{20}D$ 1.4230; found MR 26.51; calculated MR 26.71.

Found cryoscopically in benzene: M 105.7; 110.3. C_4H_7OCl. Calculated: M 106.56.

a) Determination of hydrogen chloride content. A weighed sample of the freshly prepared ether was dissolved in 25 ml of distilled water and titrated in presence of Methyl orange with 0.1 N HaOH.

Found %: HCl 34.34; 34.29. C_4H_7OCl. Calculated %: HCl 34.22.

b) Determination of chlorine content (Volhard's method). A weighed sample of the ether was dissolved in 25 ml of distilled water and titrated with 0.1 N NaOH in presence of Methyl orange. To the resulting neutral solution 25 ml of 0.1 N silver nitrate solution was added. The excess of silver nitrate was titrated with 0.1 N KCNS in presence of ferrous ammonium sulfate.

Found %: Cl 33.40; 33.45. C_4H_7OCl. Calculated %: Cl 33.29.

Synthesis of Bis-1-chloroethyl Ether. This ether was synthesized by the above-described method for the preparation of 1-chloroethyl vinyl ether and under the same conditions. A stream of hydrogen chloride was passed into 15 g of divinyl ether to complete saturation. The end of the reaction was indicated by the disappearance of the exothermic effect. The experiment lasted for four hours. Vacuum distillation gave 21 g (70%) of pure bis-1--chloroethyl ether, a clear colorless liquid, fuming in the air; b.p. 42° (10 mm); d^{20}_4 1.1285; $n^{20}D$ 1.4250; found MR 32.38; calculated MR 32.05.

Found %: M 142.6; 135.4. $C_4H_8OCl_2$. Calculated %: M 143.02.

Hydrolysis of Bis-1-chloroethyl Ether. The hydrolysis of the ether and the determination of the amount of acetaldehyde formed were carried out as in the case of divinyl ether, taking the same respective volumes of solutions. Sample of ether 0.1840 g; dilution to 250 ml. For analysis 16.51 ml of the test solution was taken. The amount of bisulfite bound corresponded to 3.13 ml of 0.1 N iodine. Hydrolysis was to the extent of 95.7%.

a) Determination of hydrogen chloride content. The analysis was carried out by the method described for 1-chloroethyl vinyl ether.

Found %: HCl 50.65, 50.60. $C_4H_8OCl_2$. Calculated %: HCl 50.99.

b) Determination of chlorine content. The analysis was carried out by the Volhard method as in the case of 1-chloroethyl vinyl ether.

Found %: Cl 49.62; 49.27. $C_4H_8OCl_2$. Calculated %: Cl 49.62.

Synthesis of Bis-1,2-dichloroethyl Ether. The synthesis was carried out in the apparatus used for the preparation of bis-1-chloroethyl ether. Divinyl ether (10 g) was placed in the flask and was cooled and stirred while a stream of dry chlorine was passed to complete saturation. The reaction temperature did not exceed 10° and was controlled by the rate of passage of chlorine. The end of the reaction was indicated by the disappearance of the thermal effect, and this coincided with the attainment of the theoretical increase in weight. The experiment lasted for four hours. Vacuum fractionation of the product gave 15 g (50%) of pure tetrachloro ether. Bis-1,2-dichloroethyl ether is a clear colorless mobile liquid with a sharp irritating odor; it fumes slightly in the air; b.p. 94-96° (7 mm); d^{20}_4 1.4805; $n^{20}D$ 1.4945; found MR 41.70; calculated MR 41.78; found M 213.3; 214; calculated M 211.93.

Found %: C 22.69; 22.57; H 2.84; 2.78; Cl 68.27; 67.83. $C_4H_6OCl_4$. Calculated %: C 22.65; H 2.85; Cl 66.95.

Synthesis of Bis-1,2-dibromoethyl Ether. The reaction was carried out in the apparatus used for the preparation of divinyl ether. Dry bromine was added from a dropping funnel to a cooled (−10°) stirred solution of 13 g of divinyl ether in 100 ml of carbon tetrachloride until saturation was complete (two hours; indicated by permanent coloration of the reaction mixture). The reaction was carried out at −5°. After removal of solvent in a vacuum, the product formed clear colorless needles. Recrystallization from absolute alcohol gave 56 g (77.4%) of the tetrabromo ether; m.p. 64°; found M 388.5; 383; calculated M 389.75. The literature gives m.p. 63-64° [4] and b.p. 142° (10 mm) [16].

Found %: C 12.46; 12.25; H 1.59; 1.59; B 81.46; 81.68. $C_4H_6OB_4$. Calculated %: C 12.32; H 1.51; B 82.03.

SUMMARY

1. A modified method for the preparation of divinyl ether is described, and some of its properties are described.

2. 1-Chloroethyl vinyl, bis-1-chloreothyl, bis-1,2-dichloroethyl, and bis-1,2-dibromoethyl ethers were

synthesized and characterized.

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Received November 9, 1956

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HETEROCHAIN POLYAMIDES

COMMUNICATION 8. SOLUBILITY OF MIXED POLYAMIDES

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In previous communications we have reported results of investigations carried out with the object of determining the relation between the structure of the macromolecule and the properties of the polymer for various heterochain polyamides [1-6]. In these we were concerned mainly with the relation between structure and the temperature characteristics of the polyamides. In the present paper we examine the relation between structure and solubility in various solvents for mixed heterochain polyamides of various types. Of the various solvents, we devoted particular attention to ethanol, because it is the most convenient solvent for many members of this class of compounds. The preparation and properties of the polyamides used in the investigation have been described in previous communications [1-6].

As the solubility of polyamides in organic solvents is generally very low, we used several methods for characterizing the relative solubilities of polyamides. Solubilities were determined qualitatively as follows. Equal amounts of the polyamides were refluxed for one hour with equal amounts (5 ml) of solvent. The solution was then rapidly filtered from the undissolved residue, and the polyamide that had dissolved was precipitated by addition of a suitable precipitant (water, ether). As the amount of polyamide in solution was very small, the relative solubilities were estimated from the turbidity produced by the precipitant. In the case of products of higher solubility, we determined the solubility quantitatively. For this purpose we took equal volumes of solutions obtained by refluxing equal amounts of polyamides in equal volumes of solvent for six hours; the solvent was then evaporated and the amounts of dry residue determined. The values obtained are not of absolute significance, because the solubility of polyamides depends on the duration of the dissolution process, the concentration of the solution, and other factors, the effects of which cannot always be estimated accurately. However, they give us an idea of the relative solubilities of the different polyamides.

In the case of polyamides of high solubility, we also determined the time during which the solution remains unchanged at ordinary temperature. This time, which we shall term the gelation time, characterizes the stability of the polyamide solution and is of interest in relation to its practical use. It is found that after a time characteristic for a given polyamide sample the solution becomes turbid and, in the case of the more concentrated solutions, turns into a stiff gel. The gelled solution can be reconverted into its original state by heating it for a short time at 40-50°.

The mixed polyamide systems that we investigated can be divided into three groups, according to the number of components*: 1) binary systems, 2) ternary systems, and 3) four-component systems. Each of these groups can itself be divided into three subgroups in accordance with the structure of the reactants used in the preparation of the mixed polyamides. Subgroup (a) includes polyamides obtained from aliphatic dicarboxylic acids and diamines.

*By "component" we understand a polyamide-forming reactant, such as a diamine salt of a dicarboxylic acid, an amino acid, or a lactam. Thus, HAd-HSeb and HAd-C are two-component systems. However, as a result of polycondensation equilibirum, which leads to an exchange of monomer units during polycondensation, a system such as HAd-PmSeb, which we regard as binary, is in fact HAd-PmSeb-PmAd-HSeb, a fact which must be taken into account in a more detailed examination of such systems.

Subgroup (b) includes polyamides obtained from aliphatic dicarboxylic acids, diamines, and amino acids or their lactams. Subgroup (c) includes polyamides obtained from aliphatic dicarboxylic acids, aliphatic diamines, and also aromatic diamines. The clearest relationships are observed in Subgroup 1a, which as already stated, comprises mixed polyamides obtained from aliphatic dicarboxylic acids and aliphatic diamines.

TABLE 1

Solubilities in Ethanol of Various Subgroup 1a Polyamide Systems

Ratio of components*	Names of components**						
	HAd/ / HSub	HAd/ / HAz	HAd/ / HSeb	HSeb/ / HAz	HA/ / HSuc	HAd/ / HGl	HAd/ / HP
1,0/0,0	i ***	i	i	i	i	i	i
0,8/0,2	i	p	i	s	i	i	i
0,6/0,4	i	s	i	s	i	i	p
0,5/0,5	—	s	p	s	—	—	—
0,4/0,6	p	s	p	s	p	p	p
0,2/0,8	i	s	i	p	p	p	p
0,0/1,0	i	i	i	i	i	i	i

* The ratio is molar. The numerator and denominator refer to the substances forming the numerator and denominator, respectively, of the expression at the head of a column under "Names of components".
** Meanings of abbreviations: Ad, adipic acid; Az, azelaic acid; Gl, glutaric acid; H, 1,6-hexanediamine; P, pimelic acid; Seb, sebacic acid; Sub, suberic acid; Suc, succinic acid.
*** i insoluble; p poorly soluble; s soluble.

Table 1 gives the alcohol-solubilities of the Subgroup 1a systems investigated.

All the polyamides given in Table 1 are readily soluble in cresol, phenol, sulfuric acid, and formic acid. For these solvents it is difficult to detect any differences in solubility among the products investigated. In the case of alcohol, however, the solubilities of these polyamides are greatly dependent on their compositions. Polyamides of the HSeb-HAz system have the highest solubilities; HAd-HAz polyamides dissolve somewhat less readily; and HAd-HSeb polyamides have still lower solubilities. Polyamides of the HAd-HSub and HAd-HSuc systems are almost insoluble in alcohol.

TABLE 2

Solubilities of HSeb-HAd Polyamides in Various Solvents

Ratio of components in system HSeb-HAd	M.p. (°C)	Solubility in				
		ethanol	2-methoxyethanol	ethanol+chloroform	cresol	benzene
1,0—0,0	210—212	i	i	i	s	i
0,8—0,2	190—195	p	p	s	s	i
0,6—0,4	170—175	s	s	s	s	i
0,5—0,5	178—180	s	s	s	s	i
0,4—0,6	180—185	s	s	s	s	i
0,2—0,8	195—198	p	p	s	s	i
0,0—1,0	250—252	i	i	i	s	i

Figure 1 shows how the solubilities of mixed polyamides of some of the systems investigated vary with composition. For each of these systems there is a clear relationship between the variation in melting point and the variation in solubility, lowering of melting point being associated with rise in solubility. Hence, in each system investigated the product of highest solubility has the lowest melting point.

As an example, in Table 2 we give solubility data for polyamides of the HAd-HSeb system in various solvents.

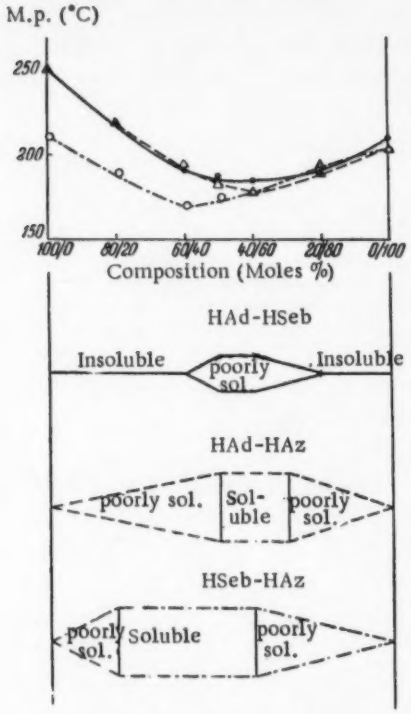

Fig. 1. Variation in melting point and in solubility in ethanol for polyamides of some binary systems: o – HAd-HSeb system; Δ – HAd-HAz system; o – HSeb-HAz system.

When we compare the solvent powers of the solvents investigated, we find that they fall in the following series of diminishing power: cresol, ethanol-chloroform mixture, ethanol, 2-methoxyethanol, 2-ethoxyethanol. These polyamides are insoluble in chloroform, benzene, and cyclohexanone.

In Subgroup 1b, which includes polyamides containing 6-aminohexanoic acid residues, three systems were investigated: HAd-C, HAz-C, and HSeb-C. Table 3 gives data on the solubility of these systems in ethanol.

It will be seen from Table 3 that mixed polyamides containing 6-aminohexanoic acid residues are somewhat more soluble than those of the preceding group. As in the case of Subgroup 1a, the polyamides are insoluble in chloroform and benzene, readily soluble in cresol, and moderately soluble in methanol, ethanol, 2-methoxyethanol, and 2-ethoxyethanol; their alcoholic solutions, obtained by heating, rapidly gel when cooled. Thus, an alcoholic solution of the HAd-C polyamide containing caprolactam at a mole fraction of 0.8 gels immediately after cooling, though a solution of the HAd-C polyamide containing caprolactam at a mole fraction of 0.6 gels only after 30 minutes. In these systems the products of lowest melting point are again those of highest solubility.

Subgroup 1c includes binary systems of polyamides in which aromatic diamine residues are present. Table 4 gives solubility data for such systems.

TABLE 3

Solubilities in Ethanol and Melting Points of Binary Polyamides Containing Caprolactam Residues

Molar ratio of components	Names of components					
	HAd/C*		HSeb/C		HAz/C	
	Solubility	M.p. (°C)	Solubility	M.p. (°C)	Solubility	M.p. (°C)
1,0/0,0	i	250—252	i	210—212	i	205—208
0,8/0,2	p	220—205	p	195—200	s	180—187
0,6/0,4	s	190—196	s	178—185	s	155—160
0,5/0,5	s	180—190	s	170—174	s	135—140
0,4/0,6	s	170—177	s	160—165	s**	130—135
0,2/0,8	s***	165—173	s	153—158	s***	135—140
0,0/1,0	p	212—215	i	212—215	i	212—215

* C = caprolactam.

** 12% solution gels in 30 minutes.

*** 12% solution gels immediately on cooling.

Table 4 shows that the replacement of aliphatic diamine residues in polyamides by aromatic diamine residues results in reduced solubility. All these products are completely soluble only in hot cresol; in the usual organic solvents they are insoluble. The system HAd-PmSeb is somewhat exceptional: it includes alcohol-soluble products, which is to be explained by the fact that it really consists of four-component polyamides. This is reflected also in the composition of the product of minimum melting point, which is different to that of the other products of this group (see Table 4). The usual correlation between high solubility and low melting point is observed also in this group.

TABLE 4

Solubilities in Ethanol and Melting Points of Polyamides Containing Aromatic Diamine Residues

Molar ratio of components	Names of components*											
	HAd/TAd		HAd/PpAd		HAd/PoAd		HAd/PmAd		HAd/PmSeb		HSeb/PmSeb	
	Solubility	M.p. (°C)	Solubility	M.p. (°C)	Solubility	M.p. (°C)	Solubility	M.p. (°C)	Solubility	M.p. (°C)	Solubility	M.p. (°C)
1,0/0,0	i	250—252	i	250—252	i	250—252	i	250—252	i	250—252	i	210—212
0,8/0,2	i	190—195	i	225—233	i	205—215	i	200—210	i	170—175	i	150—160
0,6/0,4	i	130—133	i	185—195	i	150—160	i	170—178	s	110—115	s	110—115
0,4/0,6	i	128—130	i	136—142	i	115—125	p	135—142	p	115—120	s	90—100
0,2/0,8	i	150—153	p	125—133	p	90—105	p	133—140	p	125—130	s	85— 98
0,0/1,0	i	175—176	i	260—262	i	105—110	i	258—259	i	145—150	i	145—150

*Meanings of abbreviations: T, 2,4-toluenediamine; Pp, p-phenylenediamine; Po, o-phenylenediamine; Pm, m-phenylenediamine.

In the second group of mixed polyamides, which comprises ternary systems, two subgroups were investigated. It was generally found that the solubilities of polyamides of the ternary systems investigated are greater than in the case of the binary systems.

TABLE 5

Solubilities in Ethanol and Melting Points of Polyamides of the System HAd-SHeb-HAz

No.	Relative am'ts (% by wt.) of original components of HAD-HSeb-Haz	M.p. of polymer (°C)	Solubility	
			Concentration (%)	Stability of solution
1	60÷20÷20	200—204	5	0
2	40—40—20	172—176	5	0
3	20—60—20	175—179	4	0
4	50—10—40	190—195	8	0
5	30—30—40	165—174	15	1
6	10—50—40	162—167	10	0
7	30—10—60	162—166	10	0
8	20—20—60	170—174	10	0
9	25—25—50	158—161	15	1
10	10—30—60	180—183	8	0
11	10—10—80	190—193	3	0

In Subgroup 2a we made a detailed investigation of the system obtained from the three salts HAd-HAz-HSeb (Table 5).

Fig. 2 is a diagram for this ternary system (see also Table 5) in which melting points of mixed polyamides, their solubilities, and the properties of their solutions are shown as functions of quantitative composition. The full line demarcates the region of products which gel rapidly when cooled in 8% solution. The shaded region contains products which gel after one hour in 15% solution. It should be noted that as we approach the axes the products become more and more similar in solubility to the corresponding binary systems examined previously. The highest solubilities are shown by products in the central regions of this ternary diagram.

In Subgroup 2b, which comprises ternary systems obtained with the participation of caprolactam, we investigated two systems: HAd-HAz-C and HAz-HSeb-C, the diagram for which are given in Figures 3 and 4 (Table 6).

As can be seen from Table 6 and the diagrams, the HAz-HSeb-C system includes products of very high so-

lubility. In the diagram these products are to be found in the shaded region. They are distinguished not only by their high solubility, but also by the high stability of their alcoholic solutions. Thus, the products in the shaded region of Fig. 3 give 15% solutions in alcohol which do not gel after 62 hours. In this system, as in all the preceding ones, the highest solubility is possessed by the products of lowest melting point.

TABLE 6

Solubilities and Melting Points of Polyamides of the Systems HAd-HAz-C and HSeb-HAz-C

No.	Relative amounts (% by weight) of original components	HAd-HAz-C system					HSeb-HAz-C system				
		M.p. (°C)	Solubility in ethanol		Solubility in 2-methoxy-ethanol		M.p. (°C)	Solubility in ethanol		Solubility in 2-methoxy-ethanol	
			Concl. in (%)	Stability (hours)	Concl. in (%)	Stability (hours)		conct. in (%)	Stability (hours)	conct. in (%)	Stability (hours)
1	60—20—20	175—178	5	0,3	3	0	158—162	5	1	4	0
2	40—40—20	145—148	4	0,3	3	0	145—148	5	1	3	0,5
3	20—60—20	140—144	5	0,3	3	0	145—149	5	1	3	0,5
4	50—10—40	165—169	10	12	8	2	115—118	10	20	8	6
5	30—30—40	130—133	15	36	12	18	130—134	15	70	12	24
6	10—50—40	137—140	12	24	10	2	110—113	12	30	10	'6
7	30—10—60	158—162	8	0,5	8	0	120—123	8	1	8	0,5
8	20—20—60	155—158	8	0,3	8	0	140—144	8	1	8	0,5
9	25—25—50	140—143	15	48	15	24	115—119	15	72	15	30
	10—30—60	150—154	8	0,5	8	0	140—143	8	1	8	0,5
11	10—10—80	175—178	2	0	3	0	170—174	3	0	3	0

The HAd-HAz-C system also includes products of high solubility which give stable alcoholic solutions. In Fig. 4 the shaded region contains mixed polyamides whose 15% alcoholic solutions do not gel over a period of 36 hours. This is of considerable interest, because the stability of these solutions is great enough to make their practical utilization possible.

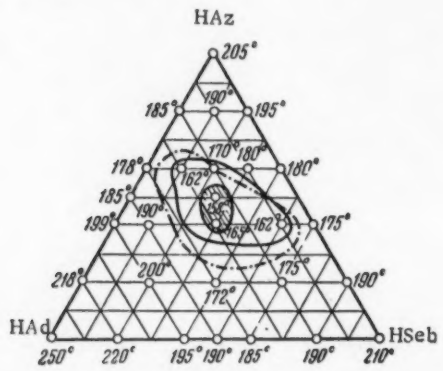

Fig. 2. Solubilities and melting points of polyamides of the system HAd-HSeb-HAz: —·— m.p. 170°; —— products giving solutions of 0.08 g in 1 ml which gel immediately on cooling; shaded region – products which in 15% solution gel after one hour.

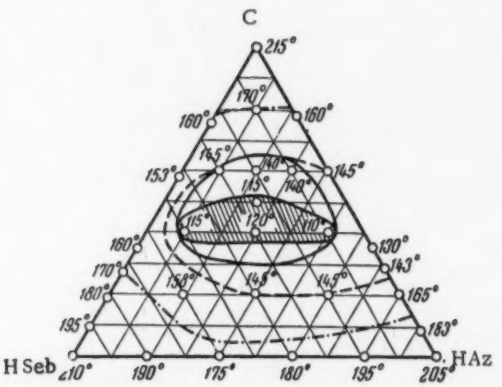

Fig. 3. Solubilities and melting points of polyamides of the system HSeb-HAz-C: — — — m.p. 145°; —·— m.p. 170°; —— products giving solutions of 0.08 g in 1 ml which are stable for one hour; shaded region – products which in 15% solution are stable for 72 hours.

In Subgroup 3b, which contains four-component mixed polyamides, we investigated some cases of the system HAd-HSeb-HAz-C. Table 7 presents solubility data for members of this system.

TABLE 7

Solubilities of Mixed Polyamides of the System HAd-HSeb-HAz-C

No.	Relative amounts of original components*	M.p. of polyamide (°C)	Solubility in				
			ethanol	ethanol + chloroform	2-methoxyethanol	2-ethoxyethanol	chloroform
1	1—1—1—1	120—125	8% solution gels on cooling	s	s	s	Swells
2	1—1—2—1	140—144	p	p	s	s	"
3	1—1—2—2	140—143	s	s	s	s	"
4	2—1—2—2	145—150	s	s	s	s	"
5	1—1—2—3	130—134	s	s	s	s	"
6	2—1—2—3	148—150	s	s	s	s	"
7	1—1—1—4	110—115	8% solution gels after 24 hours	10% solution gels after 24 hours	8% solution gels after 8 hours	8% solution gels after 24 hours	"
8	1,21—1—1—2,8	110—115	8% solution gels after 10 hours	10% solution gels after 12 hours	8% solution gels on cooling	8% solution gels on cooling	"
9	1—1—1—6	125—130	s	s	s	p	"
10	2—1—1—8	145—152	p	s	s	p	"

* The amounts are given in molecular proportions in the order HAd-HSeb-HAz-C.

** The stabilities of solutions were determined for the polymers having the highest solubilities.

Table 7 shows that products of high caprolactam content and reduced HAd content have the highest solubility. Thus, polyamides No. 7 and 8 give 8% solutions in ethanol which do not gel for quite a long time. It is interesting that these products have the lowest melting points in this series, so that the previously noted relation between solubility and melting point is observed also in the four-component system.

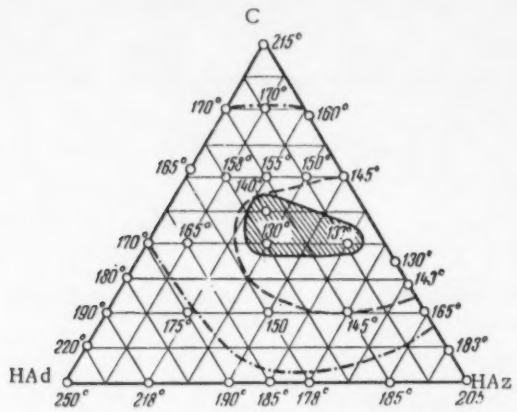

Fig. 4. Solubilities and melting points of polyamides of the system HAd-HAz-C: — — —m.p. 145°; — · — m.p. 170°; shaded region – products whose 15% solutions are stable for 36 hours.

In Subgroup 3c we investigated some cases of the systems HAd-HSeb-C-PmAd and HAd-HSeb--C-PmSeb. Table 8 shows the solubility characteristics of these systems.

It will be seen from Table 8 that introduction of the aromatic diamine into mixed ternary polyamides of the indicated compositions results in reduced solubility and simultaneous reduction in the stabilities of their solutions. Thus, whereas a 15% solution of one of the most soluble of the polyamides of the system HAd-HSeb-C (No. 1, Table 8) does not gel withing 24 hours, a solution of the same product with 10% of an additional component, the m-phenylenediamine salt, gels immediately on cooling. As the m-phenylenediamine content increases, the solubility falls. Polyamides of this system containing 60% of the m-phenylenediamine salt are almost insuluble in alcohol.

From a comparison of the relation of solubility to composition for the systems of mixed polyamides investigated, we may conclude that the solubility improves as the degree of disorder in the structure of the polyamide macromolecule increases. It is probably a general law that the products of highest solubility have the most disordered macromolecular structure. It is here interesting to note that effects of components having an odd number of carbon atoms in their chains, of which azaelaic acid appears to be particularly effective: the introduction of this component into the polyamide molecule results in a sharp increase in solubility and in the stability of alcoholic solutions of the polyamides. On the other hand, the introduction of aromatic diamines results in reduced solubility. In all the polyamide systems studied there is an antibatic relation between melting point and solubility: the most soluble products have the lowest melting points.

TABLE 8

Solubilities of Polyamides of the Systems HAd-HSeb-C-PmAd and HAd-HSeb-C-PmSeb

No.	Content* in polyamide of Pm together with equimolecular amt of acid (%)	Solubility in: ethanol		ethanol + chloroform		2-methoxyethanol		cresol	
		Name of acid added with m-phenylenediamine							
		adipic	sebacic	adipic	sebacic	adipic	sebacic	adipic	sebacic
1	0	s	s	s	s	s	s	s/c **	s/c
2	5	s	s	s	s	s	s	s/c	s/c
3	10	s	s	s	s	s	s	s/c	s/c
4	20	s	s	s	s	p	s	s/h ***	s/c
5	40	p	s	s	s	p	p	s/h	s/h
6	60	i	s	p	s	i	p	s/h	s/h
7	80	i	i	i	i	i	i	s/h	s/h

* The other components of the system were taken in constant proportions, i.e. HAd : HSeb : C = = 2 : 1 : 2, and the amount of the salt of m-phenylenediamine with adipic or sebacic acid relative to the sum of the other three components was varied.

** s/c = soluble cold. *** s/h = soluble hot.

SUMMARY

1. The relation between solubility and composition was investigated for mixed polyamides of various structures.

2. It was shown that the solubilities of the mixed polyamides were considerably greater than those of homogeneous polyamides formed from one polyamide-forming component.

3. It was shown that the effect of the composition of a polyamide on its melting point is more marked than its effect on solubility.

4. It was found that in the series of polyamides studied solvents may be placed in the following order of decreasing solvent power: phenols, alcohols, 2-methoxyethanol, 2-ethoxyethanol.

5. It was shown that, in each series, the polyamides of lowest melting point have the highest solubility: this is associated with the presence of the highest degree of disorder in the structures of these polyamides.

6. It was shown that the introduction of aromatic components into the composition of a mixed polyamide results in reduced solubility.

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Received October 10, 1956

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SYNTHESIS OF POLYALKYLENEARYLS

COMMUNICATION 3. POLYCONDENSATION OF 1,2-DICHLOROETHANE WITH FLUOROBENZENE

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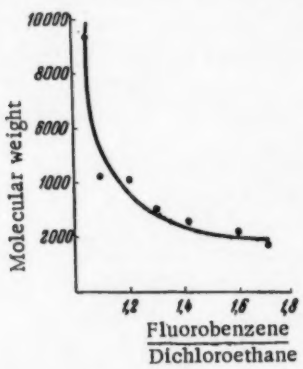
In the course of studying the polycondensation of aromatic hydrocarbons with dihaloalkanes in presence of aluminum chloride we found, in collaboration with Soboleva, that the presence of one substituent, e.g. chlorine [1] or methyl [2], in the benzene nucleus hinders the formation of three-dimensional polycondensation products. It was shown that the differing effects of these substituents on the tendency for the formation of three-dimensional polycondensation products are not associated with the sizes of the substituents, but with their orienting effects, which result in the formation of polymers that differ in structure. In order to determine the effects of the size of the substituent on the formation of three-dimensional products in the polycondensation of an aromatic hydrocarbon with 1,2-dichloroethane we undertook a study of the polycondensation of 1,2-dichloroethane with fluorobenzene in presence of aluminum chloride. Since the fluorine atom is larger than the hydrogen atom and smaller than the chlorine atom, it would be expected that a fluorine atom would create less steric hindrance to reaction than a chlorine atom.

In order to determine the effect of the relative amounts of reactants on the course of polycondensation we carried out a series of experiments in which the amounts of fluorobenzene and aluminum chloride, the temperature, and the duration of the reaction remained constant, while the amount of dichloroethane was varied. The experimental procedure was the same as that used previously [3], except that, after solvent had been distilled off, 4,4'-difluorobibenzyl and 1-fluoro-2,4-bis(2-p-fluorophenylethyl)benzene were distilled off under reduced pressure. The molecular weight of the polycondensation products were determined viscosimetrically. In the calculation of the molecular weight the constant K_m was taken to be $1.8 \cdot 10^{-4}$. The results of the experiments are shown in Table 1 and in the figure, and from these it follows that reduction in the excess of fluorobenzene leads to increase in the molecular weight of the polymer; with 5 moles per cent excess of fluorobenzene an influsible insoluble three-dimensional polymer is formed almost exclusively.



It was shown previously that the formation of three-dimensional macromolecular compounds in the polycondensation of dichloroethane with benzene [3] proceeds with a 20 moles per cent excess of benzene, whereas in the polycondensation of dichloroethane with chlorobenzene [1] three-dimensional products are formed at a 1 mole per cent excess of chlorobenzene. Fluorobenzene, therefore, occupies an intermediate position between benzene and chlorobenzene. Since the fluorine atom is intermediate in size between the atoms of hydrogen and chlorine, we may state that the tendency to form three-dimensional polymers in the polycondensation of monosubstituted benzenes with dichloroethane is the greater, the smaller the substituent. Increase in the excess of fluorobenzene in the reaction mixture leads to increase in the yield of the product of the first stage of the polycondensation (difluorobibenzyl) and to reduction in the molecular weight of the polymer. Over the molar ratios of fluorobenzene to dichloroethane taken the yield of polymer remains constant.

It was shown previously [1, 3] that, in the polycondensation of dichloroethane with aromatic hydrocarbons, the catalyst concentration affects the yield and molecular weight of the polymer. In order to determine the effect of catalyst concentration on the course of the polycondensation of fluorobenzene with dichloroethane, we carried out a series of experiments in which the amounts of fluorobenzene and dichloroethane, the temperature, and the duration of the reaction were kept constant but the aluminum chloride concentration was varied. The results of these experiments are given in Table 2.

TABLE 1

Polycondensation of 1,2-Dichloroethane with Fluorobenzene (10 moles % of aluminum chloride on the fluorobenzene; duration of reaction 4 hours)

Molar ratio fluorobenzene : dichloroethane	Yield (%)		Concentration of benzene sol. of polyethylenefluorophenyl (g/100 ml)	Specific viscosity of polyethylenefluorophenyl solution	Molecular weight of polyethylenefluorophenyl
	Difluorobibenzyl	Polyethylenefluorophenyl			
1,05	—	96,7*	3,708**	0,506	9330
1,10	5,3	75,6	2,986	0,186	4250
1,19	8,6	71,2	3,693	0,226	4190
1,30	8,2	85,1	2,018	0,088	3000
1,41	8,0	74,8	2,665	0,090	2570
1,60	12,4	73,2	2,854	0,089	2130
1,70	17,9	75,6	3,944	0,103	1770

* Consists of 10.1% of linear polymer and 86.6% of three-dimensional polymer.

** Linear polymer.

It will be seen from Table 2 that, although the polycondensation of fluorobenzene with dichloroethane does proceed at low catalyst concentrations, the yield of reaction products is low and their molecular weights are also low. With increase in the concentration of aluminum chloride the yield and molecular weight of the polymer increase and attain maxima at a catalyst concentration of 6 moles per cent on the amount of fluorobenzene; under these conditions not only soluble polymer is formed, but also a product of three-dimensional structure. Further increase in catalyst concentration leads to a shapr fall in molecular weight. The yield of polymer also falls, but to a lesser extent.

TABLE 2

Polycondensation of 1,2-Dichloroethane with Fluorobenzene (fluorobenzen : dichloroethane = 1.19 : 1; duration of reaction 4 hours; temperature 100°)

Concentration of $AlCl_3$ (moles % of fluorobenzene)	Yield (%)		Concentration of benzene sol. of polyethylenefluorophenyl (g/100 ml)	Specific viscosity of polyethylenefluorophenyl solution	Molecular weight of polyethylenefluorophenyl
	Difluorobibenzyl	Polyethylenefluorophenyl			
1,0	5,5	28,7	2,954	0,099	2 290
2,0	7,5	48,1	2,226	0,090	2 760
4,0	4,0	69,2	1,901	0,185	6 670
6,0	—	94,5*	3,728	0,655	12 050
8,0	5,5	77,0	2,917	0,201	4 680
10,0	8,6	71,2	3,639	0,226	4 190
12,0	6,6	66,3	2,205	0,097	3 000

* Consists of 41.1% of linear polymer and 53.4% of three-dimensional polymer.

We studied not only the laws governing the polycondensation of dichloroethane with flurobenzne, but also the structures of the reaction products. Possible products of low molecular weight are the isomeric difluorobibenzyls

and fluorobis[2-(fluorophenyl)ethyl]benzenes. The difluorobibenzyl was redistilled and then boiled at 95-96° (2 mm). In the cryoscopic determination of the molecular weight values of 210 and 212.5 were obtained, which are in good accord with the calculated value (218.24).

Found %: C 77.34; 77.20; H 5.56; .5.51; F 16.81; 16.71. $C_{14}H_{12}F_2$. Calculated %: C 77.06; H 5.54; F 17.40.

By the oxidation of the difluorobibenzyl with nitric acid of sp.gr. 1.1 in an autoclave at 200° for five hours, an acid of m.p. 173° was obtained. When this melting point is compared with those reported in the literature for fluorobenzoic acids it is found to correspond most closely with that of p-fluorobenzoic acid (m.p. 182°) [4]. Hence, the difluorobibenzyl formed in the polycondensation of fluorobenzene with dichloroethane is 4,4'-difluorobibenzyl, probably contaminated with the other isomers.

The fluorobis[2-(fluorophenyl)ethyl]benzene came over at 120-121° (2 mm). In the cryoscopic determination of the molecular weight values of 338.3 gna 335.4 were obtained, which are in good accord with the calculated value (340.37).

Found %: F 16.74; 16.64. $C_{22}H_{19}F_3$. Calculated %: F 16.75.

Oxidation of the product with nitric acid in an autoclave at 200° gave a small amount of fluorobenzenedicarboxylic acid, m.p. 300°, and a mixture of o-and p-fluorobenzoic acids, m.p. 119° and 180°. The literature gives 120° and 182°, respectively. A mixture melting point of the acid of melting point 119° with benzoic acid was greatly depressed, so that the acid was not benzoic acid.

Found %: F 10.64; 10.86. $C_8H_5O_4F$. Calculated %: F 10.32.

Because of the small amounts of these acids, they were not investigated more closely.

The macromolecular polycondensation product remaining after the distillation of difluorobibenzyl and fluorobis[2-(fluorophenyl)ethyl]benzene was not given any further treatment.

Found %: C 78.72; 78.90; H 5.89; 5.90; F 15.06; 15.27. C_8H_7F. Calculated %: C 78.69; H 5.76; F 15.55.

In order to determine its structure the polyethylenefluorophenyl was subjected to destructive oxidation with nitric acid of sp.gr. 1.1 in an autoclave at 200°. As a result of the oxidation we obtained a fluorobenzenedicarboxylic acid of m.p. 300°; dimethyl ester m.p. 78-79°; molecular weight, determined by titration with 0.1 N NaOH, 183.8 (duplicate 186.0), the calculated value being 184.17.

Found %: F 10.08; 10.24. $C_8H_5O_4F$. Calculated %: F 10.32.

Found %: C 56.16; 56.13; 3.89 H; 3.99; F 9.01; 8.74. $C_{10}H_9O_4F$. Calculated %: C 56.61; H 4.27; F 8.96.

Apart from 4-fluorophthalic acid, the fluorobenzenedicarboxylic acids and esters have not been described in the literature. In order to determine the structure of the fluorobenzenedicarboxylic acid obtained by the oxidation of fluorobis[2-(fluorophenyl)ethyl)benzene and of polyethylenefluorophenyl (there was no melting point depression in a mixture test on these two acids), we synthesized 4-fluoroisophthalic acid from 2,4-xylidine. The diazonium salt from 2,4-xylidine was converted into 4-fluoro-m-xylene; m.p. 140°; d^{20}_{20} 0.998; $n^{20}D$ 1.490; found MR 35.89; calculated MR 35.44.

Found %: F 15.46; 15.24. C_8H_9F. Calculated %: F 15.33.

Oxidation of 4-fluoro-m-xylene with potassium permanganate in alkaline solution gave 4-fluoroisophthalic acid, m.p. 300-301°. In the determination of the molecular weight of this acid by titration with 0.1 N NaOH values of 184.0 and 184.8 were obtained, which are in good accord with the calculated value (184.13). The dimethyl ester of this acid melted at 79°.

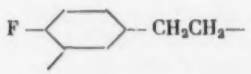
Found %: F 10.54; 10.58. $C_8H_5O_4F$. Calculated %: F 10.32.

Found %: C 56.22; 56.08; H 3.57; 3.56; F 8.91; 8.79. $C_{10}H_9O_4F$. Calculated %: C 56.61; H 4.27; F 8.96.

A mixture of the acids obtained by the oxidation of 4-fluoro-m-xylene and by the oxidation of the macro-

molecular polycondensation product of fluorobenzene with dichloroethane melted without depression at 296-297*. A mixture of the dimethyl esters of these acids melted at 75°.

On the basis of the structure of the dicarboxylic acid obtained by the oxidation of the polycondensation product of fluorobenzene with 1,2-dichloroethane in presence of aluminum chloride it may be considered that the elementary repeating unit of the polymer has the following structure:



Hence, the structure of the product of the polycondensation of fluorobenzene with dichloroethane is analogous to that of the product obtained from chlorobenzene and dichloroethane [1], and it may be called poly(3-ethylene-2--fluorophenyl).

SUMMARY

1. A study was made of the polycondensation of 1,2-dichloroethane with fluorobenzene in presence of aluminum chloride, and the main laws governing the process were determined.

2. The structure of the repeating unit was determined for the polycondensation product from fluorobenzene and 1,2-dichloroethane.

3. 4-Fluoro-m-xylene, 4-fluoroisophthalic acid, and dimethyl 4-fluoroisophthalate were prepared for the first time.

Institute of Heteroorganic Compounds of
the Academy of Sciences of the USSR

Received October 9, 1956

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*Original Russian pagination. See C. B. Translation.

BRIEF COMMUNICATIONS

DETERMINATION OF PHOSPHORUS IN NATURAL WATERS WITH THE AID OF EXTRACTION OF THE PHOSPHORUS-MOLYBDENUM HETEROPOLYACID WITH BUTYL ALCOHOL

V. G. Datsko and A. D. Semenov

The determination of biogenic elements, including phosphorus, in natural waters is of great interest for hydrochemical investigations connected with the study of the biological productivity of water reserves. The Denigé-Atkins method of determining phosphorus, which is in extensive use in hydrochemical practice, is not always sufficiently accurate and reliable. This is particularly true for waters containing colored organic substances or suspended matter; it is true also for highly mineralized waters. The rapid diminution in the intensity of the color of the reduced phosphomolybdate complex in aqueous solution makes the colorimetric determination unsatisfactory and inconvenient; in fact, in the determination of the total phosphorus content of waters containing much suspended matter the color fades so rapidly that in some cases colorimetric determination becomes impossible.

TABLE 1

Determination of Phosphates in Standard Solutions Mineralized to Various Extents

Taken (mg P per cu.m)	Added salt	Mineralization (g/liter)	Phosphates found (mg P/m³)	
			by Denigé-Atkins method	by extraction
50	NaCl	5	43	48
50	NaCl	10	39	48
50	NaCl	20	37	48
50	NaCl	35	35	47
50	NaCl	50	34	49
50	NaCl	75	32	48
25	$(NH_4)_2SO_4$	10	28	24
25	$(NH_4)_2SO_4$	25	29	24
25	$(NH_4)_2SO_4$	35	31	24
25	$(NH_4)_2SO_4$	50	34	27
25	$(NH_4)_2SO_4$	75	36	26

The method that we now propose is largely free from the defects referred to above and can be used in those cases in which the Denigé-Atkins method is unsatisfactory or impossible. The method is based on the extraction of the phosphorus-molybdenum heteropolyacid with n-butyl or isobutyl alcohol and its subsequent reduction in the alcoholic medium with stannic chloride solution; the coloration produced is estimated photometrically or visually.

EXPERIMENTAL

The phosphorus determination was carried out as follows. The solution under investigation (100 ml) was placed in a 250-ml separating funnel, and 2 ml of the usual sulfomolybdate reagent was added. n-Butyl or isobutyl alcohol (25 ml) was added, and the mixture was shaken vigorously for one minute. When the layers had separated completely, the alcoholic layer was separated and made to 25 ml with alcohol. Five or six drops of stannous chloride solution (40-50 mg of tin dissolved in 2-3 ml of concentrated hydrochloric acid, and the solution diluted to 10 ml with distilled water) were added, and after 10-15 minutes the solution was examined colorimetrically through a red filter. For visual colorimetry the separated alcohol layer was made up with alcohol to 50 ml and the colorimetry was carried out in narrow cylinders. The phosphorus content was determined from a calibration curve obtained in a similar way. Under these conditions 97-99% of the phosphates are extracted; this was confirmed by the extraction of P^{32}-labeled orthophosphoric acid from various samples of natural water and standard solutions; it was found that the degree of extraction was almost identical for waters differing in degree of mineralization. It was therefore possible to use the calibration curve for the determination of phosphates not only in fresh water, but also in mineralized waters, without introduction of a correction for degree of extraction.

For alcoholic solutions of the reduced phosphomolybdate complex there is a linear relation between phosphate concentration and absorbance in the range of phosphate contents from 0 to 100 γ / liter; moreover, in an alcoholic medium the color of the complex is more stable than in an aqueous medium; it develops during the first 10-15 minutes, and then remains almost constant for more than 90 minutes.

One of the advantages of the proposed method over the Denige-Atkins method is the possibility of determining phosphorus in highly mineralized waters without the introduction of salt corrections. Table 1 gives some examples of parallel phosphate estimations on solutions containing various amounts of sodium chloride and ammonium sulfate.

The total phosphorus content of natural waters can be determined more accurately by the extraction method. It should be noted that, in the determination of the total phosphorus content, as a result of the addition of sulfuric acid in the combustion and its subsequent neutralization with ammonia, the test sample becomes mineralized to the extent of about 5% and the effect of this on the coloration is not taken into account. Table 2 gives the results of parallel determinations of total phosphorus content by the Denigé-Atkins method and by the extraction method.

TABLE 2

Results of the Determination of Total Phosphorus Content by Two Methods

Solution investigated	Found (mg P per m^3)		Solution investigated	Found (mg P per m^3)	
	by the Denigé-Atkins method	by the extraction method		by the Denigé-Atkins method	by the extraction method
Don water	97	80	Azov Sea water		
			Sample 3	39	29
Volga water	31	22	Sample 4	73	61
			Sample 5	50	34
Azov Sea water			Sample 6	55	46
Sample 1	91	59	Taganrog Bay water		
Sample 2	60	39	Sample 1	92	55
			Sample 2	64	48

The results given in Table 1 and 2 give us reason to suppose that the Denige-Atkins method of determining total phosphorus gives somewhat high results.

In the determination of total phosphorus in waters containing large amounts of suspended mater, direct colorimetry is in some cases found to be impossible because of the rapid diminution in the intensity of the color of the reduced phosphomolybdate complex in aqueous solution, whereas determination by the extraction method gives satisfactory results.

SUMMARY

1. In the determination of phosphorus in natural waters, extraction of phosphates in the form of the phosphorus-molybdenum heteropolyacid makes it possible to avoid the introduction of salt corrections.

2. The extraction method can be used in cases in which the determination of phosphates in natural waters is impossible by the Denigé-Atkins method.

3. In the determination of total phosphorus content, the extraction method is more accurate than the Denigé-Atkins method.

Hydrochemical Institute of the Academy of Sciences of the USSR

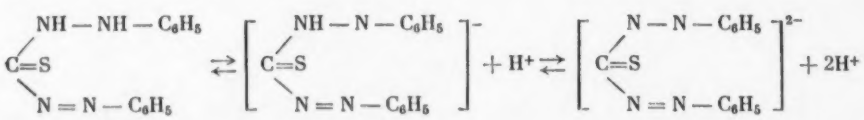
Received September 27, 1957

DETERMINATION OF SULFATE IONS BY DIRECT TITRATION WITH LEAD NITRATE WITH DITHIZONE AS INDICATOR

G. N. Nechiporenko

In volumetric methods for the determination of SO_4^{2-}, and particularly in direct-titration methods, lead salts have various advantages over barium salts as precipitants because there are analytical reagents (dithizone, diphenylcarbazone, dimethylglyoxime, alizarin, carminic acid, and others) for lead which are much more sensitive and specific than the reagents for barium ions (sodium rhodizonate, alizarin). Also, the solubility of lead sulfate can be reduced considerably by the addition of 30-40% of alcohol or acetone.

We now propose a method of determining SO_4^{2-} by direct titration with lead nitrate with dithizone as indicator. Dithizone is a weak dibasic acid, which dissociates as follows [1]:



If we denote dithizone by DH_2, we may write:

$$DH_2 \rightleftarrows DH^- + H^+ \rightleftarrows D^{2-} + H^+$$

Lead ions react with dithizone with formation of a bright-red internal-complex compound [2, 3]:

$$Pb^{2+} + 2DH^- \rightleftarrows Pb(DH)_2$$

From these equations it follows that

$$K^1_{DH_2} = \frac{[DH^-][H^+]}{[DH_2]}, \quad (1)$$

$$K_{Pb(DH)_2} = \frac{[Pb^{2+}][DH^-]^2}{[Pb(DH)_2]}, \quad (2)$$

in which $K^1_{DH_2}$ is the first dissociation constant of dithizone and $K_{Pb(DH)_2}$ is the instability constant of lead dithizonate. Solving Equations (1) and (2), we obtain

$$[Pb(DH)_2] = \frac{(K^1_{DH_2})^2}{K_{Pb(DH)_2}} \frac{[DH_2]^2[Pb^{2+}]}{[H^+]^2}. \quad (3)$$

In order to reduce the solubility of lead sulfate a 30-40% aqueous solution of acetone was used.

It will be seen from Equation (3) that the excess amount of lead ions necessary for the creation of a visually detectable concentration of lead dithizonate is proportional to the concentration of hydrogen ions.

The permissible limits of acid concentration, which are given in Table 1, depend on the concentration of the $Pb(NO_3)_2$ solution used.

TABLE 1

Permissible Concentrations of Acid

Concentration of titrated $Pb(NO_3)_2$ sol. (g-equiv/liter)	0,1	0,05	0,025	0,01	0,005
Permissible concentration limits of HCl (g-equiv/l)	0,002—0,005	0,001—0,004	0,0005—0,0003	0,0003—0,0006	0,0002—0,0004

TABLE 2

Optimum Titration Conditions

Concentration of		Volume of test sample (ml)	Amount added (ml)		Capacity of buret (ml)	Value of a division (ml)
SO_4^{2-} in investigated solution (mg/liter)	titrated $Pb(NO_3)_2$ solution (g-equiv/liter)		acetone	0.1 *N* HCl		
500 and higher	0,1	10—20	8—15	1—3	25	0,05
100—5000	0,025	5—10	5—10	0,2—0,5	10	0,02
50—2000	0,01	5—10	6—12	0,08—0,1	5	0,02
25—500	0,005	2—5	5—10	0,05—0,1	2	0,01

EXPERIMENTAL

Method of Determining SO_4^{2-} in K_2SO_4, Na_2SO_4, and $MgSO_4$ Solutions and in Natural Waters. First of all optimum titration conditions are selected (Table 2) in order to ensure adequate accuracy. If the SO_4^{2-} content of the test solution is not known, even approximately, it is necessary to use 0.025 N $Pb(NO_3)_2$ and make an approximate determination. The required volume of the test solution is taken, acetone and acid are added in the corresponding amounts (Table 2), 10 drops of indicator are added (saturated solution of dithizone in 100% acetone), and the solution is titrated with lead nitrate solution until there is a color change from bright green to red.

By this method the sulfate content can be determined accurately within 1-2%. When the Cl^- content is more than seven times as great as the SO_4^{2-} content, the probable error is increased to 3-4%. Calcium ions, even when they amount to only one-third of the weight of sulfate, interfere in the determination and must be removed by cation exchange. The presence of the following ions is permissible: Cu^{2+} up to 2 mg/liter, Co^{2+} up to 5 mg/liter, Zn^{2+} up to 20 mg/liter, Ni^{2+} up to 40 mg/liter, Fe^{3+} up to 100 mg/liter, and Mn^{2+} up to 2000 mg/liter. Hg^{2+} and Ag^+ interfere, even at 0.1 mg/liter. In the determination of sulfates in natural water it is first necessary to neutralize the water with 0.05 N HNO_3 to diphenylcarbazone. Titration is then carried out as in the case of sulfate solutions.

With the proposed method it is possible to carry out the rapid and accurate determination of sulfates in natural water containing permissible amounts of any interfering compounds. The presence of large amounts of dissolved organic substances makes the determination difficult. In waters in which the relative amounts of the principal ions are fairly constant, e.g. in sea and ocean waters, sulfates may be determined accurately within 0.5% if standards are used and constant corrections are introduced for chlorine content.

Table 3 gives a comparison of the results for the determination of SO_4^{2-} in various natural waters by the volumetric and gravimetric ($BaSO_4$) methods.

SUMMARY

1. A new method is proposed for the volumetric determination of sulfate ions; it is simple to carry out and is suitable for field conditions.

TABLE 3

Comparative Results of Determinations of SO_4^{2-} by the Gravimetric and the Proposed Volumetric Methods

Source of solution	SO_4^{2-} found (mg/liter)		Discrepancy		Contents of principal ions				
	by the volumetric method	by the gravimetric method	(mg/liter)	in %	Cl^-	$HCO_3^- + CO_3^{2-}$	$Na^+ + K^+$	Mg^{2+}	Ca^{2+}
Balkhash Lake	966	959	+7	0,8	—	—	—	—	—
Donets River	240	242	—2	0,8	—	—	—	—	—
Egorlyk River	117,1	116,5	+0,6	0,5	—	—	—	—	—
Veselov reservoir	346,5	349	—2,5	0,7	—	—	—	—	—
Proletariat reservoir	497,1	501,9	—4,8	1,0	—	—	—	—	—
Novo-Izhevo mineral water	4050	4040	+10	0,25	4210	70	—	—	520
Balata mineral water	10,62 g/kg	10,46 g/kg	+0,160 g/kg	1,5	0,931	—	3,140	1,530	0,419
Sernovodsk mineral water	1282	1296	—14	1,2	467	—	1351	30	40
Smirnovsk mineral water	709	706	+3	0,4	235	1156	626	40	262
Slavianovsk mineral water	776	781	—5	0,6	280	1310	670	—	297
Mirgorodsk mineral water	183	186	—3	1,7	1180	—	960	180	32
Normal sea water	2,646 g/kg	2,658 g/kg	—0,012 g/kg	0,5	19,372 g/kg				
Soil extract	760,9	768,5	—7,6	1,0	—	—	—	—	—
Azov irrigation system; bore hole	4395	4343	+52	1,2	—	—	—	—	—

2. By this method determinations can be made on test samples containing 0.5-50 mg of sulfate ions accurately within 1-2%.

3. The method is suitable for the rapid and accurate determination of sulfates in natural waters when the amount of chloride present is not more than seven times as great as the amount of sulfate and the amount of calcium is not more than one-third of the amount of SO_4^{2-}.

Hydrochemical Institute of the Academy
of Sciences of the USSR

Received October 7, 1957

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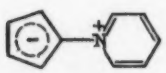
4-BENZYLPYRIDINIUM-1-CYCLOPENTADIENYLIDE

D. N. Kursanov and N. K. Baranetskaia

Until recently only three members had been described of the new class of dipolar compounds containing a negatively charged cyclopentadienyl group and known as cyclopentadienylides [1-3]. We recently prepared 1--benzylpyridiniiium-4-cyclopentadienylide (I) [4], which belongs to this class but differs from the previously known members in that the onium atom and the negatively charged grouping are not directly attached to one another.

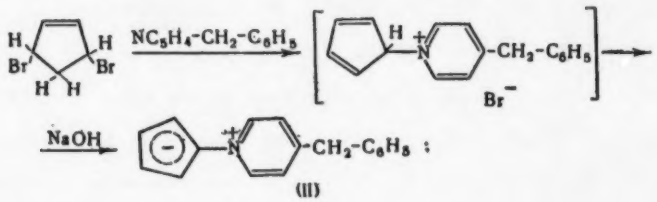
(I) (II)

We considered that it would be of interest to prepare the isomeric 4-benzylpyridinium-1-cyclopentadienylide (II), in which, in contrast to the ylide (I), the ammonium nitrogen is directly attached to the negatively charged grouping, and to compare the properties of these ylides. For the preparation of 4-benzylpyridinium-1-cyclopentadienylide (II) we used the method used by Lloyd and Sneezum [2] for the preparation of pyridinium-1-cyclopentadienylide (III):



(III)

For this purpose we treated 3,5-dibromocyclopentene with 4-benzylpyridine and treated the product with alkali. It was found that 4-benzylpyridinium-1-cyclopentadienylide (II) prepared in this way had all the characteristic properties of ylides. However, its properties were much closer to those of (III) than to those of its isomer (I). In particular, the ultraviolet absorption curves of (II) and (III) are similar in appearance and differ appreciably from the curve for the substance (I).



(II)

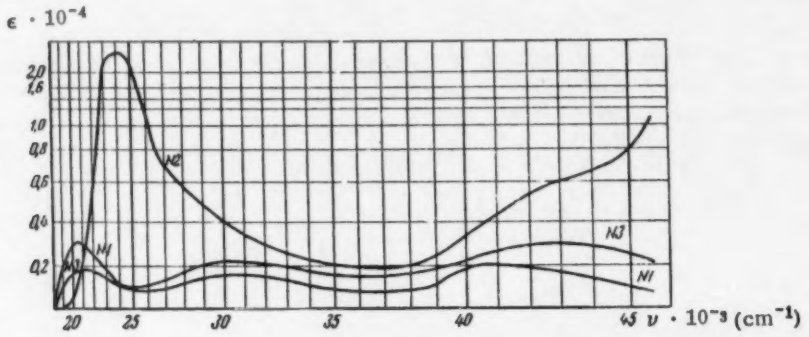
EXPERIMENTAL

A solution of 4.1 g (0.06 mole) of cyclopentadiene in 5 ml of chloroform was treated with 9.9 g (0.06 mole) of bromine in 5 ml of chloroform. The bromination was carried out in nitrogen at a temperature of from −50 to −40° [4]. The dibromocyclopentene formed was diluted with chloroform (12 ml) and 21.1 g (0.12 mole) of 4-benzyl-

pyridine* (m.p. of picrate 137-138°) was added. Reaction proceeded with evolution of heat, and cooling was therefore applied over several hours to maintain the temperature at 25°. The reaction mixture was then left for two days at room temperature. The reaction products were treated with 34 ml of 15% sodium hydroxide solution, and the precipitate was filtered off and washed with water, alcohol, and ether. Several recrystallizations from benzene led to the isolation of glistening copper-red crystals, which darkened at 100° and did not melt when heated to 250°; yield 1.8 g (12.4%).

Found %: C 87.60; 87.42; H 6.57; 6.49; N 6.16; 5.97. $C_{17}H_{15}N$. Calculated %: C 87.52; H 6.48; N 6.01.

The ultraviolet spectra were determined by I. Ia. Kachkurova in I. V. Obreimov's laboratory; we are extremely grateful to these workers.



Ultraviolet absorption spectra: 1) pyridinium-4-cyclopentadienylide; 2) 1-benzylpyridinium-4-cyclopentadienylide; 3) 4-benzylpyridinium--1-cyclopentadienylide. The spectra were taken in $1 \cdot 10^{-4}$ M ethanol solution; thickness of layer 0.5 cm.

SUMMARY

4-Benzylpyridinium-1-cyclopentadienylide was synthesized, and it was shown that it is very close in properties to pyridinium-1-cyclopentadienylide and differs considerably from its structural isomer 1-benzylpyridinium--4-cyclopentadienylide.

Institute of Heteroorganic Compounds of the Academy of Sciences of the USSR

Received October 12, 1957

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* 4-Benzylpyridine was prepared by Chichibabin's method [5]: heating of a mixture of benzyl iodine and pyridine at 270° in an autoclave. The resulting mixtures of 2- and 4-benzylpyridines were separated by fractional precipitation of their picrates.

** Original Russian pagination. See C. B. Translation.

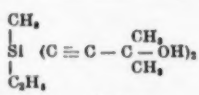
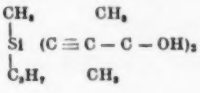
SYNTHESIS AND REACTIONS OF UNSATURATED ORGANOSILICON COMPOUNDS

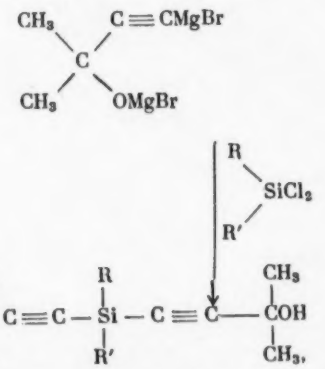
COMMUNICATION 9. SYNTHESIS OF MIXED ORGANOSILICON GLYCOLS OF THE DIACETYLENIC SERIES

I. A. Shikhiev, L. A. Kaiutenko, and E. Lukevits

The present investigation forms a further development of work on the chemistry of tertiary acetylenic alcohols [1] containing silicon [2-6]. In our previous investigations we studied ways of synthesis and the reactions of monohydric [4], dihydric [7, 2], and trihydric [6] tertiary unsaturated organosilicon alcohols of the acetylenic series. In the present paper we describe two mixed diacetylenic glycols, which we prepared as follows:

TABLE

No.	Formula of substance	M.p. (°C)	Found (%)			Calculated (%)		
			C	H	Si	C	H	Si
1		80,5—81,5	65,35 65,32	9,36 9,37	11,64 11,35	65,49	9,3	11,7
2		78—79	66,28 66,42	9,38 9,29	11,04 11,22	66,62	9,58	11,12



in which $R = CH_3$; $R' = C_2H_5$; C_3H_7.

EXPERIMENTAL

Synthesis of 4,4'-(Ethylmethylsilylene)bis[2-methyl-3-butyn-2-ol]. Over a period of three hours 84 g of 2-methyl-3-butyn-2-ol was added dropwise to a stirred cooled Grignard reagent prepared from 48.6 g of magnesium

and 218 g of ethyl bromide. On the next day stirring and cooling were continued while 71 g (0.5 mole) of dichloroethylmethylsilane was added. The reaction mixture was stirred for four hours and then left overnight. On the next day the complex was decomposed with 10-15% hydrochloric acid. The ether layer was separated and washed three times with water. Ether was distilled off, and the residue was crystallized from benzene; m.p. 80.5-81.5°.

We carried out one other synthesis by this method and so obtained the organosilicon diacetylenic glycol given with its constants in the table.

In collaboration with Dzhaforov, we have developed analogous methods of preparing organosilicon alcohols from primary and secondary acetylenic alcohols and chlorosilanes. This work will be reported in a future communication.

SUMMARY

Two mixed glycols of the acetylenic series, namely 4,4'-(ethylmethylsilylene)bis[2-methyl-3-butyn-2-ol] and 4,4'-(methylpropylsilylene)bis[2-methyl-3-butyn-2-ol], were synthesized and described for the first time.

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Received October 12, 1957

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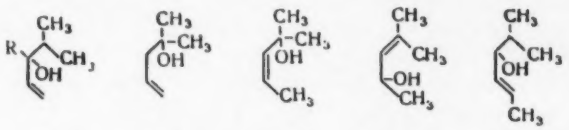
DEHYDRATION OF ETHYLENIC ALCOHOLS

I. N. Nazarov and M. V. Mavrov

In connection with our study of the diene condensations of gem-substituted butadienes of the type 4-methyl--1,3-pentadiene (i.e., 1,1-dimethyl-1,3-butadiene) and its homologs, we were faced with the task of synthesizing these dienes. Such dienes can be prepared by the dehydration of readily accessible ethylenic alcohols of type (I) (Table 1), which may be synthesized from acetylenic alcohols [1], and also other unsaturated alcohols (II)-(V), which can be prepared by methods described in the literature [2].



(I) (II) (III) (IV) (V)

TABLE 1

	R	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR	
					Result	Estimate
Ia	H	124,2—125 (742)	1,4292	0,8347	30,94	30,96
Ib	CH_3	130,7—131 (748)	1,4361	0,8393	35,48	35,58
Ic	$CH(CH_3)_2$	163—164	1,4446	0,8497	44,5	44,82

TABLE 2

Alcohol	Catalyst	Yield of hydrocarbon (% on amount of alcohol passed)	Composition* of the hydrocarbon (%)	
			unconjugated part	conjugated part
Ia	ZrO_2	81	18,VI	35,VII; 33,VIII
Ia	$AlPO_4$	85	19,2,VI	37,VII; 27,VIII
Ib	ZrO_2	82	—	30,IX; 58,X
Ib	$MgSO_4$	60	—	41,IX; 45,X
Ib	$KHSO_4$	70	—	43,IX; 44,X
Ic	ZrO_2	80	67,XIII	22,XIV
Ic	$KHSO_4$	65	56,XIII	32,XIV
Iı	ZrO_2	90	20,8,VI	40,VII; 24,VIII
II	$AlPO_4$	81	43,1,VI	22,VII; 17,6,VIII
III	ZrO_2	64	—	96,VII
IV	ZrO_2	84	—	90,VII
V	ZrO_2	85	—	60,XI; 40,XII

*Intermediate fractions, comprising 8-12%, were not taken into account.

There is an extensive literature on the dehydration of such alcohols, but much of it is contradictory. With sulfuric and hydrobromic acids, potassium hydrogen sulfate, alumina, iodine, and other substances as catalysts, conjugated dienes are formed in low yield. We have worked out a process for the vapor-phase catalytic dehydration of the unsaturated alcohols (I)-(V) over zirconia-pumice (20% zirconium dioxide) and, in some cases, over magnesium sulfate, aluminum phosphate and potassium hydrogen sulfate (10-15% by weight). The alcohols (I)-(V) were dehydrated by a single passage over the catalyst contained in a Pyrex glass tube (diameter 20 mm, length of catalyst layer 60 cm) heated in a Heraeus furnace.

Under the given conditions (300-310°; rate of passage 0.8-1.0 ml/ minute), dehydration of large amounts of alcohol (100-300 g) proceeded smoothly; the yield of hydrocarbons generally attained 80-90% in a single passage. The catalyzate was dried with magnesium sulfate and distilled. The hydrocarbon fraction was fractionated over sodium through a column having an efficiency of 39 theoretical plates.

The relative amounts of dienes obtained in the dehydration of the alcohols (Ia), (II), (III), and (IV) were determined as follows: the fraction of b.p. 56-57° ($n^{20}D$ 1.4040-1.4050), which corresponded to 2-methyl-1,4-pentadiene (VI), was readily separated in a column, and the composition of the fraction of conjugated dienes (2-methyl-1,3--pentadien (VII) and 4-methyl-1,3-pentadien (VIII)), which have close boiling points, was determined by treating this fraction (b.p. 74-76.5°; $n^{20}D$ 1.4468-1.4486) with a toluene solution of maleic anhydride at 0° [3]. 4-Methyl--1,3-pentadiene, which does not react under these conditions, was separated by steam distillation followed by distillation through a column.

In the other case mixtures of dienes were again formed: a mixture of 3,4-dimethyl-1,3-pentadiene (IX), and 2-isopropyl-1,3-butadiene (X) and a mixture of 2-methyl-2,4-hexadiene (XI) and 5-methyl-1,3-hexadiene (XII), the relative amounts of which were determined by direct fractionation through a column. Catalytic dehydration of 3-isopropyl-4-methyl-1-penten-3-ol (Ic) led, unexpectedly, to a mixture of unconjugated 3-isopropyl-2-methyl--1,4-pentadiene (XIII) and 3-isopropyl-4-methyl-1,3-pentadiene (XIV).

The results of a series of experiments on the dehydration of the alcohols (I)-(V) are given in Table 2.

Change in the temperature of the dehydration and in the rate of passage of the alcohols (Ia), (Ib), and (Ic) over zirconia had no substantial effect on the relative amounts of the isomeric dienes. Hence, catalytic dehydration does not go in the direction of the preferential formation of gem-forms of the dienes. The structures of the dienes obtained were confirmed by a study of the products of their oxidation with potassium permanganate. The physicochemical constants of the dienes (VII)-(XIV) are given in Table 3.

TABLE 3

Diene	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Ultraviolet absorption (in hexane)	
				result	estimate	λ_{max} (mμ)	ε_{max}
VII	75,8—76,5 (758)	1,4472	0,7198	30,52	28,97	228	22 400
VIII	76,2—76,7 (748)	1,4528	0,7182	30,9	28,97	234	21 000
IX	108—108,5 (747)	1,4691	0,7544	35,51	33,59	234	22 300
X	86—87	1,4324	0,7241	34,51	33,59	224	18 600
XI	110,3—110,6 (749)	1,4682	0,7452	35,87	33,59	235,5	24 000
XII	90—91	1,4358	0,7258	34,62	33,59	225	21 000
XIII	124,6—125 (738)	1,4328	0,7577	42,58	42,83		
XIV	131—132,5 (760)	1,4448	0,7504	44,02	42,83		

SUMMARY

A systematic study was made of the catalytic dehydration of 4-methyl-1-penten-3-ol (Ia), 3,4-dimethyl-1--penten-3-ol (Ib), 3-isopropyl-4-methyl-1-penten-3-ol (Ic), 2-methyl-4-penten-2-ol (II), 2-methyl-3-penten-2--ol (III), 4-methyl-3-penten-2-ol (IV), and 2-methyl-4-hexen-3-ol (V). In the course of this study methods were developed for the preparation of the following substituted gem-dimethylbutadienes: 4-methyl-1,3-pentadiene (VIII), 3,4-dimethyl-1,3-pentadiene (IX), 2-methyl-2,4-hexadiene (XI), and 3-isopropyl-4-methyl-1,3-pentadiene (XIV).

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Received October 15, 1957

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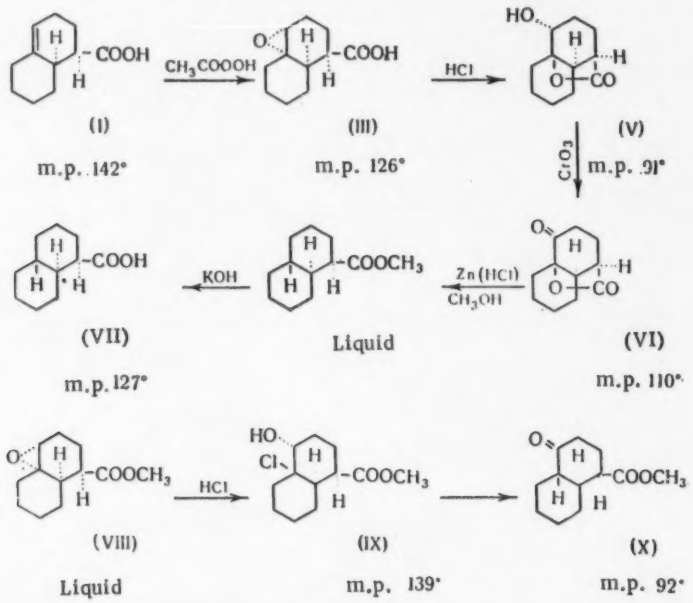
*Original Russian pagination. See C. B. Translation.

STEREOCHEMISTRY OF THE OXIDATION OF 1,2,3,5,6,7,8,8a-OCTAHYDRO--1-NAPHTHOIC ACIDS

V. F. Kucherov, G. M. Segal', and I. N. Nazarov

As already shown [1], the catalytic hydrogenation of the isomeric 1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acids proceeds stereoselectively with addition of hydrogen from the side opposite to that of the screening carboxy group. It was of interest to study the stereochemistry of the oxidation of such acids with peroxyacetic acid and osmium tetraoxide, because these methods, as well as possibly proving the configurations of decahydronaphthoic acids, permit the stereospecific synthesis of 4-keto derivatives, obtained previously by diene condensations with 1-(1-acetoxyvinyl)cyclohexene [2,3].

Our investigations showed that oxidation of syn- and anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acids (I) and (II) with peroxyacetic acid give good yields of the corresponding α-epoxides (III) and (IV), in which the epoxy ring is disposed on the side opposite to the carboxy groups. Such a configuration for the α-epoxides was proved by a series of stereospecific transformations, which permitted at the same time the synthesis of the stereoisomeric decahydro-4-oxo-1-naphthoic acids. It was found that, when treated with hydrogen chloride, the α-epoxide (II) readily underwent trans-diaxial lactonization with formation of the 4-hydroxy-γ-lactone (V), which was oxidized to the corresponding 4-oxo-γ-lactone (VI); this was subjected to Clemmensen reduction and then hydrolysis with formation of the previously described [2] trans-syn-decahydronaphthoic acid (VII).

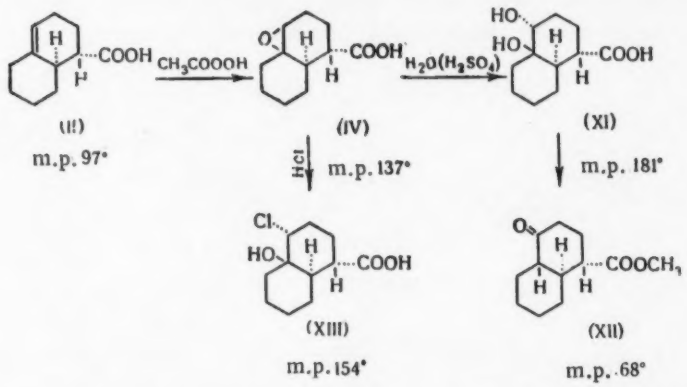


* The isomeric epoxides in which the epoxy ring is on the same side as the 1-carboxy are referred to as β-epoxides. With the object of uniformity in the writing of formulas, the representation of the original syn- and anti-octahydronaphthoic acids and their transformation products are conventionally referred to isomers corresponding to a given optical form.

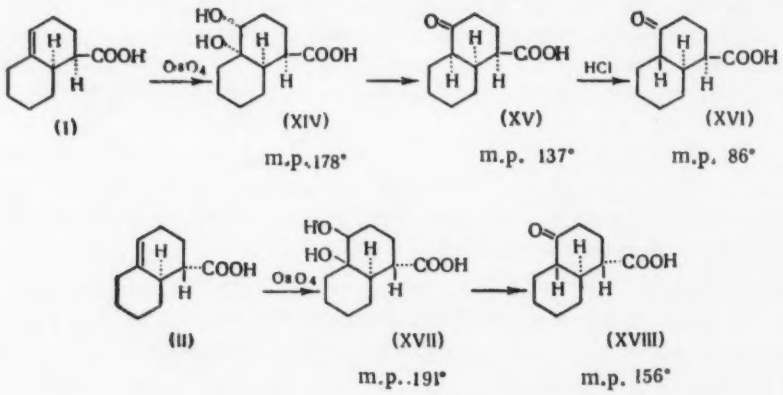
Opening of the epoxy ring in the lactonization of the α-epoxide (III) proceeds from the side of the C–O bond at C-4a, because the corresponding α-epoxy ester (VIII) was found to give a trans-chlorohydrin (IX) having a chlorine atom at C-4a when treated with hydrogen chloride; the structure of (IX) was proved by reduction with zinc in acetic acid [4] and subsequent oxidation to the trans-syn 4-keto ester (X). As an examination of molecular models shown, all the transformations described can occur only if the epoxy ring has an α-configuration.

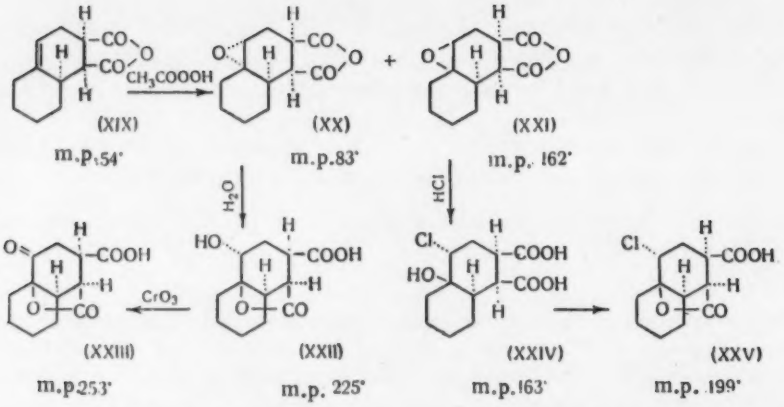
In accordance with its configuration, the isomeric α-epoxide (IV) is hydrolyzed to the trans glycol (XI), which is incapable of lactonization and is dehydrated when heated with p-toluenesulfonic acid to the trans-anti 4-keto ester (XII).

When treated with hydrogen chloride, the α-epoxide (IV) is converted into the trans chlorohydrin (XIII), which has its chlorine atom at C-4, so that it is incapable of dehalogenation under the action of zinc and acetic acid. All these transformations, when considered in relation to molecular models, show that the epoxy ring in the epoxide (IV) has the α-configuration and that its scission occurs at the C–O bond at C-4.

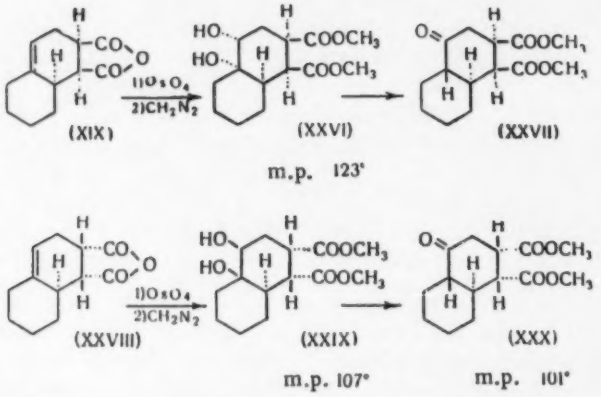


In a similar way, oxidation of the isomeric acids (I) and (II) with osmium tetraoxide also proceeds from the side opposite to that of the carboxy groups. As a result of the cis-hydroxylation reaction, the syn acid (I) is converted into the cis glycol (XIV), which is readily dehydrated under the action of p-toluenesulfonic acid into the cis-syn 4-keto acid (XV); isomerization of (XV) with hydrochloric acid gives the trans-syn 4-keto acid (XVI). As follows from the configuration of the anti acid (II), its cis-hydroxylation leads to the isomeric cis glycol (XVII), which is dehydrated to the previsouly described [2] trans-anti 4-keto acid (XVIII).





The oxidation of syn-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic anhydride (XIX) with peroxyacetic acid, unlike that of the monocarboxylic acids, proceeds sterically in a nonspecific manner and, as a result of addition in both possible directions, it gives a mixture of equal amounts of the isomeric α- and β-epoxides (XX) and (XXI).



In accord with the above-described transformations, the α-epoxide (XX) is readily lactonized with formation of the 4-hydroxy-γ-lactone acid (XXII), which is oxidized to the previously described [5] 4-keto-γ-lactone acid (XXIII). On the other hand, the isomeric β-epoxide (XXI) undergoes scission of the epoxy ring at the 4-C—O when treated with hydrogen chloride and gives the trans chlorohydrin (XXIV), which lactonizes to the 4-chloro-γ-lactone acid (XXV). This transformation shows that the original epoxide (XXI) has the β-configuration, because only in this case can trans-diaxial opening of the epoxy ring at the C—O bond at C-4 lead to a trans chlorofhydrin capable of ready lactonization.

In contrast to peroxyacetic acid oxidation, the cis-hydroxylation of the octahydronaphthalenedicarboxylic acids with osmium tetraoxide proceeds stereospecifically. As was shown in the case of the syn-cis anhydride (XIX), oxidation with osmium tetraoxide with subsequent esterification gives only the cis glycol (XXVI), dehydration of which readily gives the trans-syn-cis 4-keto ester (XXVII), m.p. 94°.

The hydroxylation of the cis-anti anhydride (XXVIII) proceeds similarly with formation of the isomeric cis glycol (XXIX), which is dehydrated by p-toluenesulfonic acid to the trans-anti-cis 4-keto ester (XXX). These transformations proceed in good yield and can provide a convenient method for the synthesis of isomeric cyclic keto dicarboxylic acids of given configuration.

SUMMARY

It was shown that the oxidation of syn- and anti-1,2,3,5,6,7,8,8a-octahydro-1-naphthoic acids with peroxy-

acetic acid and with osmium tetraoxide proceed stereospecifically from the side opposite to that of the carboxy group. On the other hand, the oxidation of syn-cis-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid goes in both of the possible sterically different directions with formation of isomeric α- and β-epoxides.

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Received October 16, 1957

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*Original Russian pagination. See C. B. Translation.

INVESTIGATIONS ON BORON COMPOUNDS

COMMUNICATION 1. SYNTHESIS OF TRIALLYLBORINE

A. V. Topchiev, A. A. Prokhorova, Ia. M. Paushkin, and M. V. Kurashev

Saturated organoboron compounds have been the most thoroughly studied. It is only recently that methods for the preparation of unsaturated boron compounds have been described and their physicochemical properties have become known [1-3]. With regard to triallylborine, the only reference to this compound appears in a patent [4], according to which it can be prepared by reaction between triallyl borate and allylmagnesium bromide. Triallylborine is obtained in 33% yield.

In this paper we described methods of preparing triallylborine from boron trifluoride and allylmagnesium bromide, from boron trichloride and allylmagnesium bromide, and from boron trifluoride and allylmagnesium chloride. In order to avoid the formation of by-products [5, 6] in the preparation of the Grignard reagent from allyl halide and magnesium, the preparation of triallylborine was carried out in one stage, i.e., without prior preparation of allylmagnesium bromide.

EXPERIMENTAL

Reaction of Boron Trifluoride with Allylmagnesium Bromide. A 500-ml four-necked flask fitted with stirrer, thermometer, capillary for the passage of nitrogen dropping funnel, and reflux condenser was charged with 28.6 g of magnesium and 250 ml of dry ether. Air was pumped from the system, which was then filled with carefully purified nitrogen. A few drops of allyl bromide were added to the magnesium turnings and ether; when reaction set in, a mixture of 95 g of allyl bromide and 21 g of freshly distilled ether complex of boron trifluoride was added dropwise with stirring. When the addition was complete, the reaction mixture was stirred further for one hour. Ether was then distilled from the mixture in a stream of nitrogen at atmospheric pressure, heat being applied by means of an oil bath at 80-100°. Distillation was continued under reduced pressure (15 mm), and at an oil-bath temperature of 150-170° a clear colorless liquid, which was spontaneously inflammable in the air, came over; b.p. 65-70° (15 mm); yield 85%. It was redistilled with collection of the fraction coming over at 62-65° (15 mm); yield 80%; d^{20}_4 0.7178; bromine value 340 (calculated 358.2); molecular weight 134 (duplicate 136) (calculated 134).

Found %: C 80.16; H 11.39; B 8.45. $(CH_2 = CH - CH_2)_3B$. Calculated %: C 80.6; H 11.19; B 8.21.

When triallylborine is treated with bromine, addition of the bromine to two of the allyl groups proceeds fairly readily, reaction being complete within 30 minutes. Addition of bromine to the third allyl group proceeds much less readily: in the course of ten days only 95% of the theoretically possible amount of bromine had reacted. It should be noted that, in work with triallylborine in presence of small amounts of oxygen, a polymeric substance is formed containing not only boron, carbon, and hydrogen, but also oxygen.

Reaction of Boron Trifluoride with Allylmagnesium Chloride. Reaction as described above between 12.8 g of magnesium turnings covered with 250 ml of dry ether, 19 g of freshly distilled boron trifluoride etherate, and 50 g of allyl chloride in 50 ml of dry ether gave 1.5 g (10%) of triallylborine (fraction of b.p. 62-65° (15 mm)).

Found %: C 80.70; H 11.50; B 7.8. $(CH_2 = CH - CH_2)_3B$. Calculated %: C 80.60; H 11.19; B 8.21.

The physicochemical properties of the product were the same as those of the product of the first experiment.

Reaction of Boron Trichloride with Allylmagnesium Bromide. The experimental procedure and the treatment of the reaction mixture were the same as in the previous experiments. Reaction between 24 g of magnesium turnings covered with 250 ml of dry ether, 80 g of allyl bromide, and 12.9 g of boron trichloride gave 1.5 g (10%) of triallylborine (fraction of b.p. 62-65° (15 mm)).

Found %: C 80.60; H 11.30; B 8.1. $(CH_2=CH-CH_2)_3B$. Calculated %: C 80.60; H 11.19; B 8.21.

The physicochemical properties of the product were the same as in the first experiment.

SUMMARY

A method is proposed for the preparation of triallylborine by reaction between boron trifluoride and allylmagnesium bromide; the desired product is obtained in 80% yield.

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Received October 16, 1957

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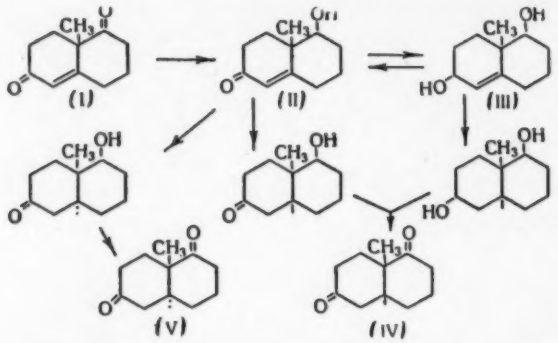
SYNTHESIS OF 4,4a,5,6,7,8-HEXAHYDRO-5-HYDROXY-4a-METHYL-2(3H)-NAPHTHALENONE

I. N. Nazarov and I. A. Gurvich

In our laboratory we have previously developed a convenient synthesis of 3,4,8,8a-tetrahydro-8a-methyl--1,6(2H,7H)-naphthalenedione (I), which is an interesting intermediate product in the synthesis of steroids [1]. The corresponding hydroxy ketone (II) is also an important intermediate product in the synthesis of triterpenoids and polycyclic compounds allied to the steroids. This hydroxy ketone has been prepared in five stages from 3,4--dihydro-6-methoxy-1(2H)-naphthalenone, but in practice this method is not very convenient [2]. Recently, by the microbiological reduction of the naphthalenedione (I) it was found possible to obtain the diastereoisomers of the hydroxy ketone (II) [3]. In the present paper we described a new preparative method for the synthesis of the hydroxy ketone (II): reduction of the naphthalenedione (I) with sodium borohydride.

It was found that, as a result of the selective reduction of the 1-keto group, reduction of the naphthalenedione (I) with one equivalent of sodium borohydride gives the hydroxy ketone (II) in one stage in a yield of up to 50%. When (I) is reduced with two equivalents of sodium borohydride, both keto groups are reduced and the diol (III) is formed in a yield of more than 85%; this diol is smoothly oxidized by manganese dioxide to the hydroxy ketone (II). Under mild conditions such oxidation touches only allylic alcohol groupings with formation of α,β-unsaturated ketones, and it provides a proof of the structure of the hydroxy ketone (II). This method for the preparation of the hydroxy ketone (II) is an extremely convenient one.* The presence in (II) of an α,β-unsaturated ketone grouping was confirmed by the ultraviolet absorption spectra of the hydroxy ketone itself and its 2,4-dinitrophenylhydrazone. The infrared absorption spectrum of the diol (III) has a very intense band at 1054 cm^{-1}, which indicates an equatorial disposition of hydroxy groups and also the presence of α-hydroxy in the hydroxy ketone (II).



As would be expected, in the catalytic hydrogenation of the hydroxy ketone (II) and the diol (III), there is preferential formation of cis-decahydronaphthalene derivatives, which was proved by their oxidation to known cis--hexahydro-8a-methyl-1,6(2H,7H)-naphthalenedione (IV).

In the reduction of the hydroxy ketone (II) with lithium in liquid ammonia, the main product is the corresponding

*Similar methods of preparing the hydroxy ketone (II) were developed simultaneously with ours and were published recently [6].

trans-decahydronaphthalene derivative, because its oxidation with chromium trioxide gives the known trans-hexahydro-8a-methyl-1,6(2H,7H0-naphthalenedione (V) [4].

EXPERIMENTAL

1,2,3,4,6,7,8,8a-Octahydro-8a-methyl-1,6-naphthalenediol (III)

Sodium borohydride (2.4 g) was added slowly to a cooled stirred solution of 9.2 g of 3,4,8,8a-tetrahydro-8a-methyl-1,6(2H,7H)-naphthalenedione (I) in 160 ml of alcohol. Solvent was distilled off, 70 ml of water was added to the residue, and 8 g of the diol (III) separated; m.p. 147-148° (from acetone): ν 1054, 1026 cm^{-1}.

Found %: C 72.44; 72.45; H 9.74; 9.91. $C_{11}H_{18}O_2$. Calculated %: C 72.49; H 9.95.

4,4a,5,6,7,8-Hexahydro-5-hydroxy-4a-methyl-2(3H)-naphthalenone (II).

a) A solution of 85 mg of $NaBH_4$* in 17 ml of alcohol was added dropwise to a stirred solution of 1 g of the diketone (I) in 35 ml of alcohol at 0°. The reaction mixture was stirred further for 50 minutes, after which one drop of acetic acid was added. Alcohol was distilled off, 5 ml of water was added, and the reduction product was extracted with ether. The product, amounting to 0.75 g, was an oil, and in chromatography on alumina the benzene and ether fractions gave an oil that crystallized on addition of water. The crystals of the hydrate of the hydroxy ketone (II) (0.5 g) melted at 59-60°, which is in accord with the literature [2]; λ_{max} (in alcohol) 241 mμ (logϵ 4.133); 314 mμ (logϵ 1.825). The 2,4-dinitrophenylhydrazone of the hydroxy ketone (II) had m.p. 176-177° (from aqueous alcohol); λ_{max} (in alcohol) 387 mμ (logϵ 4.528).

Found %: N 15.60; 15.4. $C_{17}H_{20}O_5N_4$. Calculated %: N 15.5.

b) A solution of 8 g of the diol (III) in 150 ml of dry chloroform was shaken for 14 hours with 35.4 g of finely ground manganese dioxide prepared by a previously described method [5]. The chloroform solution was filtered, and the residue was washed with chloroform. Chloroform was distilled off and left a residue of 6.5 g of an oil, which solidified on addition of a drop of water; m.p. 58-49°. In admixture with the hydroxy ketone obtained in Experiment (a) there was no depression of melting point.

Hydrogenation of the Diol (III) and the Hydroxy Ketone (II)

a) The diol (III) (1.3 g) was hydrogenated in alcoholic solution in presence of platinum oxide; 160 ml of hydrogen was absorbed. The resulting oil was oxidized with chromium trioxide in acetic acid. After removal of solvent and chromatographic treatment, the benzene fraction yielded 0.5 g of cis-hexahydro-8a-methyl-1,6(2H,7H)-naphthalenedione (IV), m.p. 64-65° (undepressed by admixture of a known sample).

b) The hydroxy ketone (II) (0.4 g) was hydrogenated under the same conditions (48 ml of hydrogen was absorbed). Oxidation of the hydrogenation product and chromatography gave 100 mg of the cis diketone (IV), m.p. 62-63° (undepressed by admixture of a known sample).

Reduction of the Hydroxy Ketone (II) with Lithium in Liquid Ammonia

A solution of 1.5 g of the hydroxy ketone (II) in ether was added to a solution of 0.5 g of lithium in 100 ml of liquid ammonia. After 50 minutes, dry ammonium chloride was added to the reaction mixture until it was decolorized. The usual treatment gave 1 g of oil, which was oxidized with chromium trioxide. After the chromatography the benzene fraction gave 0.3 g of the trans diketone (V), m.p. 53-54° (undepressed by admixture of a known sample).

SUMMARY

New preparative methods were developed for the synthesis of 4,4a,5,6,7,8-hexahydro-5-hydroxy-4a-methyl-2(3H)-naphthalenone (II) from 3,4,8,8a-tetrahydro-8a-methyl-1,6(2H,7H)-naphthalenedione (I).

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Received October 26, 1957

* A preparation containing 85% of $NaBH_4$ was used.

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*Original Russian pagination. See C. B. Translation.

CATALYTIC TRANSFORMATIONS OF DIALKYLCYCLOHEXANES IN PRESENCE OF HYDROGEN UNDER PRESSURE

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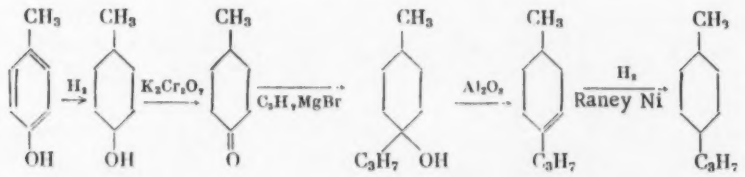
Many investigations have been carried out on the transformations of cyclohexane hydrocarbons in presence of hydrogen under pressure [1-5]. It was shown that, in presence of a platinized alumina catalyst, cyclohexane, methylcyclohexane, and ethylcyclohexane undergo not only dehydrogenation, but also partial isomerization into cyclopentanes with subsequent hydrogenolysis into normal and branched paraffins. There are no references in the literature to the transformations of cyclohexane hydrocarbons having substituents with chains of more than two carbon atoms, nor to the transformations of disubstituted hydrocarbons.

In the present investigation we examined the catalytic transformations of 1-isopropyl-4-methylcyclohexane and 1-methyl-4-propylcyclohexane with the object of determining the main directions of reaction, and also the effect of carriers on the character of these transformations.

EXPERIMENTAL

1-Isopropyl-4-methylcyclohexane and 1-methyl-4-propylcyclohexane were synthesized as follows:



The products were distilled through a column of 70-plate efficiency; they had the following properties. 1-Isopropyl-4-methylcyclohexane: b.p. 170.2° (750 mm); $n^{20}D$ 1.4395; d^{20}_4 0.8009. (the literature [6] gives b.p. 170.7°, $n^{20}D$ 1.4395 and d^{20}_4 0.8008. Trans-1-methyl-4-propylcyclohexane: b.p. 171.2° (740 mm); $n^{20}D$ 1.4359; d^{20}_4 0.7910; cis-1-methyl-4-propylcyclohexane: b.p. 174-174.5° (753 mm); $n^{20}D$ 1.4404 and d^{20}_4 0.8003. According to the literature [6], a mixture of cis- and trans-1-methyl-4-propylcyclohexanes boils over the range 174.3-177.1° and has $n^{20}D$ 1.4393 and d^{20}_4 0.7966. Experiments on the transformations of these hydrocarbons were carried out in a flow-type apparatus at 450° under a pressure of 20 atm of hydrogen in presence of 0.5% Pt–Al_2O_3, 0.5% Pt–ZrO_2, and pure Al_2O_3 and ZrO_2. The hydrocarbons were passed at a space velocity of 0.5 $hour^{-1}$ at a molar ratio of hydrogen to hydrocarbon of 4 : 1. The catalyzates were submitted to precision fractionation through a column of 40-plate efficiency, and the compositions of the fractions isolated were determined by chemical methods and by Raman spectrum analysis.*

The fractional compositions of the catalyzates are given in Tables 1-3.

SUMMARY

1. At 450° in presence of hydrogen at 20 atm and 0.5% Pt–Al_2O_3, 1-methyl-4-propylcyclohexane is con-

*The Raman spectra were measured by Iu. P. Egorov, to whom the authors express their great indebtedness.

verted into p-propyltoluene, toluene, o-, m-, and p-xylenes, ethyltoluenes, and ethylxylenes. Under these conditions pure alumina alone also brings about the dehydrogenation and dealkylation of dialkylcyclohexanes to a small extent.

TABLE 1

Fractional Composition of the 1-Methyl-4-propylcyclohexane Catalyzate Obtained in Presence of 0.5% Pt–Al_2O_3

No.	B.p. (°C at 748 mm)	n_D^{20}	d_4^{20}	Content (% by wt. on catalyzate)	Composition of fraction
1	110,2—110,8	1,4967	0,8675	5,5	Toluene
2	110,8—150	1,4960	0,8656	6,6	Toluene, o-, m-, and p-xylenes
3	150—180,8	1,4952	0,8678	8,8	p-Ethyltoluene with some o- and m-ethyltoluenes
4	180,8—183,8	1,4948	0,8600	36,5	p-Propyltoluene
5	183,8—189	1,4992	0,8716	8,8	Ethylxylenes
6*	62—65	1,3824	0,6695	13,8	Unidentified paraffins
7	65—160	1,4095	0,7337		

*Fractions 6 and 7 were first separated from the mixture of aromatic hydrocarbons by chromatographic adsorption on silica gel.

TABLE 2

Fractional Composition of the 1-Methyl-4-propylcyclohexane Catalyzate Obtained in Presence of 0.5% Pt–ZrO_2

No.	B.p. (°C at 745 mm)	n_D^{20}	d_4^{20}	Content (% by wt. on catalyzate)	Composition of fraction
1	172,2—176	1,4378	0,7975	11,7	1-Methyl-4-propylcyclohexane
2	181,5—183	1,4946	0,8581	74,3	p-Propyltoluene

TABLE 3

Fractional Composition of the 1-Isopropyl-4-methylcyclohexane Catalyzate Obtained in Presence of Pure Al_2O_3 and ZrO_2

No.	Catalyst	B.p. (°C at 745 mm)	n_D^{20}	d_4^{20}	Content (% by wt. on catalyzate)	Composition of fraction
1	Al_2O_3	109,5—110,8	1,4962	0,8664	4,6	Toluene
2		168—170,2	1,4390	0,8003	84,4	1-Isopropyl-4-methylcyclohexane
3		176—181	1,4903	0,8568	6,8	*p*-Methylcumene
4	ZrO_2	169,5—170,2	1,4395	0,8012	95,2	1-Isopropyl-4-methylcyclohexane

2. Platinized zirconia brings about only the dehydrogenation of the cyclohexane ring.

3. 1-Methyl-4-propylcyclohexane was prepared in its cis and trans forms for the first time.

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Received October 28, 1957

*Original Russian pagination. See C. B. Translation.

**In Russian.

POSSIBILITY OF THE POLYMERIZATION OF ETHYLENE IN PRESENCE OF LITHIUM HYDRIDE, ALUMINUM HALIDE, AND TITANIUM TETRACHLORIDE

A. V. Topchiev, I. M. Tolchinskii, and B. A. Krentsel'

In one of his papers Ziegler [1] states that heating of an ethereal solution of lithium aluminum hydride with ethylene at 180-200° under pressure results in the formation of a mixture of α-olefins: butene, hexene, decene, and dodecene. On the basis of the experimental data it may be considered that the actual catalyst in this case is aluminum tetraethyllithium, formed by the action of ethylene on lithium aluminum hydride:

$$LiAlH_4 + 4C_2H_4 \rightarrow LiAl[C_2H_5]_4$$

The formation of macromolecular ethylene polymers was not observed in these experiments.

On the other hand, it is known that triethylaluminum (which in form of its complex with titanium tetrachloride is a catalyst for the polymerization of ethylene, even at atmospheric pressure) may be obtained from lithium hydride with intermediate formation of lithium aluminum hydride and aluminum hydride:

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl;$$

$$3LiAlH_4 + AlCl_3 \rightarrow 4AlH_3 + 3LiCl;$$

$$AlH_3 + 3C_2H_4 \rightarrow Al[C_2H_5]_3.$$

In view of this, it was of interest to investigate the possibility of the simultaneous formation of triethylaluminum and the polymerization of ethylene to polyethylene as an essentially one-stage process.

The experiments* were carried out in an autoclave in an inert solvent (white spirit, n-octane, or n-heptane). The original ethylene contained 99.7% of C_2H_4 and 0.3% of air. The gas was freed from oxygen by means of copper turnings at about 300° and then purified and dried with soda-lime, fused calcium chloride, and granulated alumina. Nitrogen, which was used as the inert gas necessary for work with organometallic compounds, was purified similarly. Lithium hydride was used in a finely ground form. As aluminum halide both the chloride and bromide were used. We now give the results of some of the most characteristic experiments.

Experiment 4. The solvent was n-octane. The over-all concentration of the catalyst in the solvent was 5% by weight. The realtive weights of catalyst components were:

$$LiH : AlCl_3 : TiCl_4 = 1 : 6 : 4.$$

The pressure was 10 atm, and the temperature 80°. Polymer in the form of a white powder was obtained in a yield of 40.3 g per liter of solvent. The molecular weight of the polymer, determined from the intrinsic viscosity in decahydronaphthalene at 130°, was 50,000; its melting point was 130°.

Experiment 6. The solvent was white spirit, dried with calcium chloride and distilled twice over sodium. The concentration of catalyst in the solvent was about 5%. The relative weights of catalyst components were 1 : 11 : 4. The pressure in the autoclave was 10 atm, and the temperature 85°. The yield of polymer, a white powder, was 236 g per liter of solvent. The molecular weight of the polymer was 87,000, and its melting point was 140°.

*Senior laboratory worker E. A. Mushina took part in the experimental work.

It must be mentioned that the polymerization of propene was carried out similarly at LiH : $AlCl_3$: $TiCl_4$ = = about 1 : 6 : 0.5. The yield of polypropylene varied from 45 to 82 g per liter of solvent.

An important feature of the polymerizations of ethylene and propene in the way described is that lithium hydride and also the lithium chloride formed in the reaction are insoluble in the solvents employed. Better results are therefore obtained by the use of aluminum bromide (instead of the chloride), which gives the more soluble lithium bromide during the reaction. The lithium bromide does not cover the surface of the hydride that has not yet reacted, and conditions are therefore favorable for the more complete utilization of the hydride.

We have already pointed out above that lithium aluminum hydride must be formed as an intermediary, and that this reacts with excess of aluminum halide with formation of aluminum hydride, which gives triethylaluminum in the process of the polymerization of ethylene. The activity of lithium aluminum hydride was proved in special experiments, in which lithium aluminum hydride was used in place of lithium hydride and the corresponding amount of aluminum halide. Polymerization then went satisfactorily at a higher temperature (about 140°). The yield of polymer was 120 g per liter of solvent, and its molecular weight was 10,000-12,000. The polyethylene prepared in the ways described was of very high dispersity, and samples of it were processed satisfactorily into a foam product of high quality.

SUMMARY

1. It was shown that it is possible to prepare polyethylene in presence of lithium hydride, aluminum halide, and titanium tetrachloride.

2. A suggestion is made concerning the possible mechanism of the reaction.

3. It was shown that polypropylene can be obtained similarly.

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Received October 28, 1957

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INVESTIGATION OF THE STRUCTURE OF PEPTIDES CONTAINING GLYCINE AND L-PROLINE

N. S. Andreeva, V. I. Iveronova, T. D. Kozarenko, K. T. Poroshin, V. A. Shibnev and N. E. Shutskever

The study of peptides containing imino acid residues are of great interest for the investigation of protein structure. The stereochemical part played by pyrrolidine rings in the configuration of the polypeptide chain is not yet adequately clear. It is known that imino acid residues are not arranged in simple α-spirals, and they may therefore be regarded as one of the sources of disturbances in the regular spiral configuration of the polypeptide chain. It has been suggested that the bends in polypeptide chains which make it possible for the chains to be packed into globules occur at proline and hydroxyproline residues. Also, collagens, which are very rich in imino acid residues, have an extremely specific configuration of chains, the basis of which is still obscure. All this points to the necessity for investigating the stereochemistry of the sections of peptide chains containing proline rings.

The structures of peptides and polypeptides derived from many α-amino acids are being investigated at present. However, very little work has been done on compounds containing imino acid residues. Up to now complete structural investigations have been carried out on only two compounds containing imino acids: on L-hydroxyproline [1, 2] and on L-leucyl-L-prolylglycine [3]. Our own work concerns the sterochemistry of peptides of glycine and L-proline. The sequences glycine-proline and proline-glycine are characteristic of proteins of the collagen group [4] and also for other proteins [4]. In the present paper we report the results of preliminary x-ray investigations.

EXPERIMENTAL

Glycyl-L-proline was synthesized in 66.7% yield (calculated on the L-proline) from benzyloxycarbonylglycine and L-proline by methods described in the literature [6, 7]; m.p. 184° (with decomposition); $[\alpha]^{20}D$ −112.8° (in water). Crystals of glycyl-L-proline precipitate from an alcoholic solution containing a little ether. Such a solution was placed in a refrigerator until nucleus crystals had formed, and the further growth of these was allowed to proceed at room temperature. After 7-10 days colorless crystals had formed as plates with the main face in the (100) plane; their dimensions were 0.5 × 0.2 × 0.1 mm. The crystals were very hygroscopic; they included many twinned crystals and concretions.

L-Prolylglycine monohydrate was synthesized in 37% yield (calculated on the L-proline) from benzyloxycarbonyl-L-proline and glycine by the method described in the literature [8]; m.p. 236° (with decomposition); $[\alpha]^{20}D/H$ −19.8° (in water). Crystals precipitate from aqueous solution when alcohol is added until a slight turbidity appears. The crystals grow under the same conditions as in the case of glycyl-L-proline, but somewhat more rapidly (3-4 days). The crystals are colorless and have a well developed (100) face; dimensions: 0.3 × 0.2 × 0.1 mm.

L-Prolylglycine is much less hygroscopic than glycyl-L-proline. Twinned crystals and concretions are often met.

Benzyloxycarbonylglycyl-L-proline was prepared in 77.5% (calculated on L-proline) by the method described in the literature [6]; m.p. 156-157°; it crystallizes from water in colorless needles, 3 × 0.5 × 0.5 mm.

Glycyl-L-proline anhydride was prepared by heating glycyl-L-proline ethyl ester at 105° at 10^{-3} mm pressure for eight hours; m.p. 203-213°; $[\alpha]^{20}D$ −217.4° (in water). It was purified by vacuum sublimation from a thin layer by a method developed previously [9]; the process was carried out at 150° and $2 \cdot 10^{-3}$ mm. Crystals of

glycyl-L-proline anhydride precipitate from methanol when dry ether is added to the saturated solution; colorless needles 5 × 0.5 × 0.5 mm.

For the synthesis of dipeptides we used L-proline, $[\alpha]^{20}D$ −87° (from water), isolated from gelatin by the rhodanilate method [10].

The faces of all the crystals were imperfect, so that it was impossible to carry out goniometric measurements. For all crystals we determined the dimensions of the elementary cell, the Bravais lattice, and the space group by x-ray diffraction methods. All the results are given in the table. The low density of benzyloxycarbonylglycyl--L-proline should be noted; it is to be explained by the looseness of packing of the molecules in this space group.

TABLE

Substance	a (A)	b (A)	c (A)	β	z	ρ_{expt}	ρ_{theor}	Space group
Glycyl-L-proline	10,45± ±0,05	11,45± ±0,05	6,65± ±0,04	110°	4	1,42	1,52	$P2_1$
L-Prolylglycine	6,59± ±0,03	5,45± ±0,03	12,89± ±0,05	100,5°	2	1,23	1,35	$P2_1$
Glycyl-L-proline anhydride	5,38± ±0,03	9,62± ±0,04	12,89± ±0,05		4	1,47	1,52	$P2_12_12_1$
Benzyloxycarbonyl-glycyl-L-proline	9,35± ±0,04		36,4± ±0,4		4	0,60	0,64	$P4_12_1$ or $P4_32_1$

In conclusion we express our thanks to V. N. Rogulenkova for the investigation of the benzyloxycarbonyl-glycyl-L-proline crystals.

SUMMARY

1. Glycyl-L-proline, L-prolylglycine, benzyloxycarbonyl-L-proline, and glycyl-L-proline anhydride were synthesized and were obtained in the form of monocrystals.

2. The first stage of the x-ray structure analysis of the synthesized compounds was carried out.

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Received October 31, 1957

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CATALYST SELECTIVITY

COMMUNICATION 1. REDUCTION OF MESITYL OXIDE AND CROTONALDEHYDE OVER A ZINC CATALYST

L. Kh. Freidlin, A. S. Sultanov and M. F. Abidova

We showed recently that skeletal zinc has high catalytic activity for the reduction of aldehydes and ketones to alcohols at atmospheric pressure, but is inert in the hydrogenation of unsaturated compounds. In the present work we have found that a zinc catalyst shows the same selectivity toward C=O and C=C bonds present in one and the same molecule. These facts are of great interest for catalysis.

It is known that, in presence of hydrogenation catalysts, hydrogen generally adds in the first place at the C=C bond, though it may add simultaneously at C=C and C=O. Only one exception has been noted [1]. By the addition of measured amounts of ferric sulfate and zinc acetate it was found possible to suppress the hydrogenating function of the catalyst (platinum oxide, platinum black) toward the C=C bond. However, this catalyst is complex and not readily available. The activity of zinc in these reduction reactions with molecular hydrogen is observed already at low temperatures. It is probable that zinc has a catalytic effect also in the reduction of aldehydes and ketones with active hydrogen obtained by the action of acid or caustic alkali on zinc.

EXPERIMENTAL

The catalyst was prepared by leaching turnings of a 50% Zn–Al alloy with 3% aqueous sodium hydroxide until about 90% of the aluminum had been removed (as calculated from the volume of hydrogen evolved). The reaction was carried out under continuous-flow conditions. The temperature was measured in the catalyst layer. The volume of catalyst was 125 ml; the height of the layer was 150 mm. The content of carbonyl groups in the catalyzate was determined by the oxime method, and the content of unsaturated compounds was determined from the amount of hydrogen consumed in the hydrogenation of a weighed amount of product in presence of Raney nickel in 96% ethanol at 20°. It was shown by separate experiments that under these conditions the CO groups of mesityl oxide and crotonaldehyde are not reduced. The original mesityl oxide had b.p. 58-60° (60 mm) and $n^{20}D$ 1.4425.

It will be seen from Table 1 and the figure that at 45-87° the ketone content of the catalyzate fell sharply whereas its unsaturation remained unchanged. It follows that at these temperatures only one process occurs:

$$(CH_3)_2C=CHCOCH_3 \xrightarrow[Zn]{+H_2} (CH_3)_2C=CHCHOHCH_3. \quad (I)$$

The yield of 4-methyl-3-penten-2-ol attained 80%. At higher temperatures the carbonyl content of the catalyzate began to increase and the content of C=C bonds fell. This indicates simultaneous isomerization of the 4-methyl-3-penten-2-ol formed:

$$(CH_3)_2C=CHCHOHCH_3 \xrightarrow[Zn]{} (CH_3)_2CHCH_2COCH_3 \quad (II)$$

It was shown by a special experiment that 4-methyl-3-penten-2-ol is indeed isomerized to 4-methyl-2-pentanone when passed in a stream of nitrogen at 125° over the zinc catalyst at the usual space velocity. The catalyzate was found to contain 35.6% of ketone, calculated as 4-methyl-2-pentanone, and 68.5% of the original unsaturated alcohol.

The increase by 4.1% is explained by the fact that the alcohol used contained 4% of mesityl alcohol. In Experiments 6 and 7 the sum of unsaturated compounds and ketones in the catalyzate is clearly less than 100%. This indicates the subsequent reduction of the unsaturated ketone formed in stage (II):

$$(CH_3)_2CHCH_2COCH_3 \xrightarrow[Zn]{+H_2} (CH_3)_2CHCH_2CHOHCH_3. \qquad \text{(III)}$$

Hence, with rise in temperature the process becomes more complex and three substances may be formed simultaneously in the catalyzate.

TABLE 1

Experiment	Temp. (°C)	Content (% by weight) in the catalyzate of		Composition of catalyzate (% by weight)			
		ketones*	unsaturated compounds*	Mesityl oxide	4-Methyl-3-penten-2-ol	4-Methyl-2-pentanone	4-Methyl-2-pentanol
1	45	96,0	100,0	93	4	0	0
2	60	59,6	100,0	58	38	0	0
3	75	16,3	100,0	16	79	0	0
4	87	15,3	100,0	15	80	0	0
5	100	28,4	86,0	14	69	13	0
6	125	55,0	36,5	0	34	53	8
7	150	56,0	32,8	0	32	54	10

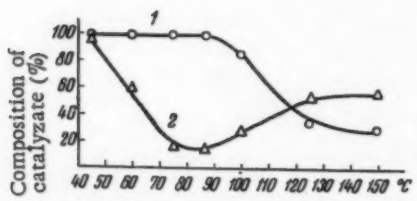
* Calculated on mesityl oxide.

TABLE 2

Experiment	Temperature (°C)	Content (% by weight) in the catalyzate of		Composition of catalyzate (% by weight)		
		aldehydes*	unsaturated compounds*	Crotonaldehyde	2-Buten-1-ol	Butyraldehyde
1	60	85,7	100,0	82	11	0
2	80	80,5	100,0	74	18	0
3	100	74,0	89,6	61	25	9
4	120	86,0	78,5	61	14	21

* Calculated on crotonaldehyde.

The analytical results enable us to make tentative calculations of the compositions of the catalyzates formed at various temperatures. We now give two examples of these calculations. In Experiment 5 at 100° we found 86% of unsaturated components, i.e., mixture of mesityl oxide and 4-methyl-3-penten-2-ol. The remaining 14% must be attributed to stage (II). As the total amount of ketones formed in this experiment was 28.4%, the amount of mesityl oxide was 14.4%. Subtracting the 14.4% of mesityl oxide from the total amount of unsaturated compounds in the catalyzate, we find that 71.6% of unsaturated alcohol was formed. In calculations on the data of Experiment 6 we assumed that at 125° and higher mesityl oxide reacts almost completely. Hence, the carbonyl content of the catalyzate determines the yield of 4-methyl-2-pentanone (55%), and the content of unsaturated compounds determines



Reduction of mesityl oxide at various temperatures. Content in catalyzate of 1) unsaturated compounds; 2) ketones.

the amount of unsaturated alcohol formed (36%). The remaining 9% is evidently 4-methyl-2-pentanol.

The unsaturated alcohol of the 75° and 87° catalyzates was brought into combination with boric acid in ether; other substances were distilled off, and the complex was then decomposed with sodium bicarbonate. Separation, drying, and distillation gave a substance of boiling point 128-130°. Its unsaturation was 100%, but some ketone (mesityl oxide) was present (4.3%). These properties correspond to 4-methyl-3-penten-2-ol [2]. Fractionation of the 125° and 150° catalyzates gave a fraction of b.p. 115-117° and $n^{20}D$ 1.3985, corresponding to 4-methyl-2-pentanone. Its semicarbazone melted at 128° (not recrystallized); the literature gives m.p. 132° [3]. Its 2,4-dinitrophenylhydrazone melted at 93-94°; the literature gives m.p. 95° [3].

The original crotonaldehyde had b.p. 101-103°; $n^{20}D$ 1.4350; purity according to unsaturation 100%, and according to carbonyl content 99%. From the analytical results the compositions of the catalyzates obtained at various temperatures were calculated.

As will be seen from Table 2, at 60° and 80° the unsaturation of the catalyzate did not change but the aldehyde content fell. At these temperatures only the carbonyl group was reduced. The 100° catalyzate was found to contain 78.5% of unsaturated compounds, i.e., a mixture of crotonaldehyde and 2-buten-1-ol. The remaining 21.5% of unsaturated component must be attributed to saturated butyraldehyde. As the total amount of aldehyde formed was 86%, the amount of crotonaldehyde must have been 64.5%. Subtracting 64.5% from the total amount of unsaturated compounds in the catalyzate, we find that 14.0% of unsaturated alcohol was formed.

The results given in Tables 1 and 2 are slightly lower than the calculated values because they have been recalculated as per cent of the amount of materials passed.

SUMMARY

1. Taking the cases of mesityl oxide and crotonaldehyde as our examples, we have shown that a zinc catalyst has the unique property of catalyzing the reduction of a carbonyl group without touching a C= C bond when reaction is at atmospheric pressure and low temperatures.

2. At 100° and higher the reaction is complicated by the isomerization of the unsaturated alcohol formed into a saturated ketone.

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Received December 10, 1957

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LETTER TO THE EDITOR

ELECTRON PARAMAGNETIC RESONANCE IN THE SYSTEM $R_3Al-TiCl_4$

The systems AlR_3-TiCl_4 and AlR_3-TiCl_3 have recently acquired great interest because of their use as initiators in a peculiar form of the polymerization of olefins recently discovered by Ziegler. It may be supposed that the primary reaction between the molecules present in the initiator consists in a bimolecular reaction with formation of a free radical: $R_3Al + TiCl_4 \rightarrow R + AlClR_2 + TiCl_3$. According to Semenov's views, such a reaction, if it is not too endothermic, should proceed readily with a very small activation barrier. In itself this reaction cannot be regarded as responsible for the initiation of the process, because polymerization initiated by a mixture of AlR_3 and $TiCl_4$ is in many ways different from the usual free-radical polymerization. In particular, it appears to give a heterogeneous character. It may be supposed, however, that the primary formation of free radicals affects the nature of the heterogeneous catalyst formed. We have, in fact, observed electron paramagnetic resonance with a g factor of about 2 in the brown precipitate formed in the reaction of trialkylaluminums with titanium chlorides in octane solution.

In the case of the system $Al(i\text{-}C_4H_9)_3-TiCl_4$, resonance absorption is observed at room temperature. The products of the reaction of $TiCl_4$ with $Al(C_2H_5)_3$ and $TiCl_3$ with $Al(C_2H_5)_3$ can also give paramagnetic resonance, which in this case was observed at the temperature of liquid nitrogen and was not observed at room temperature. The presence of resonance absorption probably indicates the presence of radicals or of complexes of radical character in the systems studied, because none of the reactants taken separately (including dry $TiCl_3$ in octane) shows resonance absorption under the conditions of the experiment. We may suppose that these radicals are associated in some peculiar way with the polymerization process.

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Received January 9, 1958

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

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